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THE ELEMENTS

OF

PHYSICAL CHEMISTRY

BY

J. LIVINGSTON R. MORGAN, Ph.D.

Professor of Physical Chemistry in Columbia University

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FIFTH EDITION, REVISED AND ENLARGED

FIRST THOUSAND

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PREFACE TO THE FIFTH EDITION

In this edition not only is the size of the volume increased, but much of the text has also been rewritten, in order that the reader may the more readily visualize the various phenomena described, and correlate the various relationships presented.

Owing to the existence of special works dealing with problems taken from the subject of Physical Chemistry, the number of problems presented for solution in Chapter X has not been very materially increased, although greater care has been exercised in their selection; so that they illustrate now more perfectly and completely than before, the most valuable quantitative applications of the subject. The discussions of the phase rule, and of the subject of colloidal solutions, have also been decidedly restricted, considering their importance; for special works on both subjects are now at hand, and the subjects themselves are entirely too large to warrant even an attempt to adequately treat them in any such general text as this is intended to be.

The mathematical derivation of the various relationships of physical chemistry, as presented here, is in all cases as simple as possible, and is simply intended to show the reader that the laws derived are plausible, and in accord with a general, theoretical, view-point. For rigid derivations, accordingly, some one of the numerous works on thermodynamics must be consulted. The law itself, together with its limitations from even the most rigid form of derivation, however, is accentuated in every case, and made as clear as possible by description, and the application of it to numerical problems.

The system of notation employed in the text has been changed throughout, in order that it may agree with that recently adopted by the International Commission for the Unification of Physico-Chemical Symbols. (Proc. Chem. Soc., **29**, 333–339, 1913.)

J. L. R. M.

June, 1914.

PREFACE TO THE FIRST EDITION

The object of this book is to present the elements of the entire subject of Physical Chemistry in one volume, together with the important and but little known applications of it to the other branches of chemistry. Many persons have found it difficult to obtain a comprehensive outline of the subject, owing to the length of time which it has been necessary to spend upon the separate volumes devoted to special portions of it. To all such this volume may be of value.

It is especially intended as a text-book for either class-work or self-instruction, and although the calculus is used in the derivation of some of the laws, still much can be done without any training in the higher mathematics. In general, references are given, so that any one wishing to make an extended study of any special portion may do so with little difficulty. The amount of the subject included, however, embraces that which is likely to be useful to all chemists, and is that which is being given to all chemical students at Columbia University.

No claims of originality are made for the major portion of the text, for Ostwald's Lehrbuch der allgemeinen Chemie and Analytical Chemistry, as well as Le Blanc's Electrochemistry and Nernst's Theoretical Chemistry, have been very freely used. Some things, however, will be found in a new form, which it is hoped is simpler and clearer than the usual one

The arrangement as well as the scope of the volume is new, which I think makes the subject more logical and clear.

J. L. R. M.

DEPARTMENT OF PHYSICAL CHEMISTRY,
HAVEMEYER LABORATORY,
COLUMBIA UNIVERSITY
December, 1898.

PREFACE TO THE SECOND EDITION

In preparing this edition, I have endeavored to do three things: first, to bring the subject-matter itself up to date; second, to make, wherever possible, the relations clearer than before; and third, to render the book itself more useful to those studying the subject without an instructor. The physical meaning of all relations is shown, so that those who have not sufficient mathematical training to actually derive the single relations will at least understand them and be able to apply them when necessary. Many things found superfluous in the old edition have been omitted and a number of new relations added. Following the advice of Prof. Ostwald, the chapter on the rôle of the ions in analytical chemistry has been given a place in Chapter VII between chemical equilibrium and kinetics. In Chapter X a collection of problems is given which will show the value and application of each important relation considered. This collection, I think, will be particularly acceptable to those studying alone, as well as to others who have already studied the subject but not yet attempted to apply it.

December, 1901.

PREFACE TO THE THIRD EDITION

As a basis for the revision of this work I have been so fortunate as to have a copy of the former edition containing suggestions and criticisms from the hand of Prof. Ostwald. For his great kindness in having volunteered to take this trouble, and for many other favors, both during my student days and since, I am indeed very grateful, and I cannot allow this opportunity to pass without expressing to him, as far as words may suffice, my sincerest thanks. Further, I wish to acknowledge the influence of his "Vorlesungen über Naturphilosophie," some points of which I have attempted to apply in this edition.

The ideas I have had in mind in making this revision may be summarized as follows: To bring the subject-matter up to date; to distinguish sharply between hypothesis and fact, avoiding the former as far as it is possible; and to accentuate the physical meaning of the results of mathematical reasoning, i.e., to employ mathematics simply as a means to an end, and to make the matter as intelligible as possible, even to the non-mathematical reader. In few words the motive, if I may so express myself, of this edition is to treat the subject as something which can be applied to other branches, and to illustrate the application and methods of application by the use of numerous problems. In this way it is hoped that the subject, instead of being merely a more or less interesting theoretical study, as is too often the case, may appeal to the student as a tool, by the aid of which *actual results* may be obtained. This plan is the expression of the need of my own students, and I assume consequently that it will be welcome to others who not only wish to *know* the subject, but also to *use* it.

May, 1905.

PREFACE TO THE FOURTH EDITION

All the changes made in this edition have been undertaken with the view of bringing the subject-matter up to date and making the various relations more intelligible to the average, non-mathematical, reader. To this end, and to retain the approximate size of the volume, the more unnecessary portions of the other editions have been omitted, and in all cases the physical meaning of the derived relations has been given immediately after the derivation, in order that those who cannot follow the derivation may at least be able to use in practice the results obtained from it. The sections on "indicators" and "general analytical reactions" have been omitted, for they are now presented in all the better text-books on analytical chemistry.

June, 1908.

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ELEMENTS OF PHYSICAL CHEMISTRY

CHAPTER I

INTRODUCTORY REMARKS

Physical Chemistry *is that branch of science which has for its object the study of the laws governing chemical phenomena.*

Other titles for this subject are also in use (General Chemistry, Theoretical Chemistry), but, since the subjects treated lie in that border-land between Physics and Chemistry, and since many purely physical methods are used, the term Physical Chemistry is the most descriptive one, and is to be preferred. The subject of Physical Chemistry is usually divided into two parts: Stoichiometry and Chemical Energy, the latter term including the laws of affinity and all other allied subjects. As it is difficult, however, to make a sharp distinction, we shall consider both together, dividing the subject only into minor portions in the form of chapters.

Energy.—Since much of our work has to do with the different forms of energy, it will be well to recall here some things which later we shall use constantly.

Force is whatever changes, or tends to change, the motion of a body by altering its direction or its magnitude. The unit of force is the dyne. A dyne acting upon a gram for one second will give it the velocity of 1 centimeter per second, and n dynes, n centimeters per second. At Washington a body falling freely for one second acquires the velocity of 980.10 centimeters, therefore the force of gravitation of 1 gram at Washington is equal to 980.1 dynes.

Work.—The unit of work is that work which is done when unit force is overcome through unit distance. This is called the erg. We have then

$$\text{dynes} \times \text{centimeters} = \text{ergs}.$$

The maximum work to be obtained from any process is that amount which can be produced under ideal conditions.

Energy is work or anything which can be transformed into work, or produced from work.* Mechanical energy is of two kinds, kinetic and distance—the former being due to motion, the latter to position. As all forms of energy can be transformed the one into the other, the general unit of energy is the erg. Since it is impossible to remove all the energy from a body, we have no way of determining how much is contained in it. We can only measure the excess of energy which a body contains in a given state over that which it contains in a certain standard state. This is determined by allowing a body to go from the given state to the standard state in such a way that the difference in energy all appears in a measurable form, for example, as heat. If we measure this heat, we have the energy of the body in the given state, as compared to that in the normal state.

Atomic and molecular weights.—Since we are to make very extensive use of the atomic and molecular weights in our later work, it is quite necessary here to make clear the exact meaning of the words, as we shall employ them. A glance at the practical application of the concepts shows that there is nothing hypothetical about them, other than the derivation of the words. It is unfortunately true, however, that from this one early acquires the idea that the actual results of an analysis or chemical reaction are dependent not only upon the *practical work*, but also upon the *molecular* or *atomic hypothesis*. This idea is so strong, indeed, that it is not uncommon to find people assuming that any direct proof contrary to the hypotheses would actually affect the practical results themselves. It is not possible to discuss this question in detail here, so the reader must be referred elsewhere.* The definition of the two terms, however, will serve to show that they are simply expressions of experimentally determined facts, and in such a sense they are used throughout this book.

---

* See Ostwald's Vorlesungen über Naturphilosophie. Second edition, p. 158.

In order that a similar confusion may be avoided with the other concepts, which are introduced later in our work, we shall always *define each concept in terms of experiment*, for then there can be no question as to whether it is hypothetical (susceptible to neither proof nor disproof), or a theory (which can be proven or disproven by further experiments) or a law (which has been proven by past experiments).

The *molecular* or *formula weight* in the gaseous state (that in other states will be defined later) expresses the *number of units of weight of gas which under like conditions of temperature and pressure occupy the same volume as 32 units of weight of oxygen, or 2 units of weight of hydrogen;* i.e., approximately 22.4 liters at 0° and 760 mm. pressure, when the unit of weight is taken as the gram; or a corresponding volume at any other temperature or pressure. Since the factor for the conversion of grams into ounces (avoirdupois) (0.0353) is the same as that for the conversion of liters into cubic feet, this relation also holds for ounces and cubic feet. In other words, the molecular weight of any gas, expressed in ounces, occupies the volume of 22.4 cubic feet at 0° and 1 atmosphere pressure.

---

* See Ostwald, l. c.

The *atomic* or *combining weight* of any element is the weight which combines with 16 units of weight of oxygen, or some multiple or submultiple of that; or, is the weight which combines with 1 gram of hydrogen, or some multiple of it.

A much simpler definition of atomic or combining weight applicable to the states in which the molecular or formula weight can be determined by direct experiment, is the following: *The atomic or combining weight is the smallest weight of an element which is found to exist in the molecular or formula weight of any compound.*

CHAPTER II

THE GASEOUS STATE*

Definition of a gas.—A gas is distinguised by its property of infinite expansion. In other words, a gas is limited in volume only by the walls of the vessel which contains it.

The gas laws.—The so-called gas laws, derived below, are the result of experience as to the behavior of gases in general under varying conditions.

Boyle's (or Mariotte's) law: At constant temperature the volume of any gas is inversely proportional to the pressure under which it exists.

If v represents the volume of any definite weight of a gas at the pressure p, and v_1 the volume of the same weight of the gas at the pressure p_1, then, according to this law,

$$pv = p_1 v_1 = \text{constant, for constant temperature.}$$

If the temperature is different in the two cases, the product pv is no longer equal to the product $p_1 v_1$.

The effect of a change in temperature upon the volume of a gas held at constant pressure is given by the *law of Charles (or of Dalton, or of Gay-Lussac): The volume of any gas increases by the 1/273 part of its volume at 0° C. for every increase of its temperature equal to 1° C.* In other words, the volume-change of the gas per degree is not 1/273 times its volume at that particular temperature, *but 1/273 times the volume it would occupy at 0°.*

---

* For numerical problems involving the principles discussed in this chapter, see Chapter X.

If the temperature were decreased continuously from 0°, according to this law, then, we would finally reach a point at which the volume of the gas would be equal to zero. Provided the law of Charles holds for such a low temperature, this point will be 273 centigrade degrees below 0° C., for the loss in volume at that point will be 273/273 parts of the volume which was unity at 0°. This point is called the *absolute zero*, and the temperature measured from it in centigrade degrees is the *absolute temperature.* This absolute temperature is designated by the letter T, the temperature according to the centigrade scale being distinguished by the letter t. Between these two terms, then, we have the relation

$$T=t+273, \quad \text{or} \quad t=T-273.$$

The volume of a gas is thus proportional to its absolute temperature, provided its pressure remains constant; and, by Boyle's law, *its pressure is proportional to the absolute temperature, when its volume remains constant.* From this we can now find the value of the product pv for any temperature. We have

$$v \propto T \quad (p=\text{const.}),$$

$$v \propto \frac{1}{p} \quad (T=\text{const.});$$

hence

$$v \propto \frac{T}{p}$$

and

$$v=k\frac{T}{p}$$

or

$$pv=kT.$$

But at 0° C.

$$p_o v_o = k273,$$

and, combining these two equations, with elimination of the constant k, which was used to transform the variation into an equality, we find

$$pv = \frac{p_o v_o}{273} T;$$

or when we assume that we start with the specific amount of 1 gram of the gas

$$pv_s = \frac{p_o v_{s,o}}{273} T,$$

where v_s and $v_{s,o}$ are respectively *the specific volumes of the gas* at T and p_1, and at 0° C. (273° absolute) and the standard pressure, p_o. As this term $\frac{p_o v_{s,o}}{273}$ is a constant for any one gas, since all its terms under such a condition are constant, it is usually called *the specific gas constant*, and designated by the letter r. We have, then

$$pv_s = rT,$$

r having a characteristic value for each gas.

When instead of considering the volume of 1 gram of gas we start with the volume of the molecular weight in grams, i. e., of the mole,* the above equation is transformed into

$$pv_m = \frac{p_o v_{m,o}}{273} T,$$

---

* From here on we shall call the molecular weight in grams *the mole*, as has been suggested by Ostwald. A mole of any gas at 0° and one atmosphere pressure occupies 22.4 liters, which is the average results of many determinations on different gases.

where $v_m = Mv_s$, and $v_{m,o} = Mv_{s,o}$; i.e., are the volumes of the mole under these conditions.

In this form, *since the mole of all gases occupies the same volume at the standard pressure p_o and at 0° C.*, we observe that not only is the term $\frac{p_o v_{m \cdot o}}{273}$ constant for any one gas, but that *it is also constant for all gases.* Designating $\frac{p_o v_{m \cdot o}}{273}$ by the letter R, we have then as *the equation of state* for all gases

$$pv_m = RT, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where $R \left(= \frac{p_o v_{m,o}}{273} \right)$ is called *the molecular gas constant, and has an identical value for all gases.*

Comparison of the two equations above, the one for the specific volume, and the other for the molecular volume, shows plainly that *the specific gas constant of any gas must be inversely proportional to its molecular weight;* for, since $Mv_s = v_m$, and $Mv_{s,o} = v_{m,o}$, Mr must be equal to R, independent of the nature of the gas—i.e., *the product of the specific gas constant into the molecular weight of the gas is always equal to R, a constant.* The smaller the molecular weight, therefore, the larger must be the specific gas constant, for only then could the product be equal to the same, constant, value in all cases.

Since the gas constants, both for the specific and for the molecular quantities, are energy quantities, for pressure times volume is equal to work, and T is a pure number, we can calculate their numerical values, *provided we select for p and v such units as will give a product in some recognized energy units.* The units possible to use here are pressures in grams per square centimeter—volumes in cubic centimeters; pressures in atmospheres—volumes in liters; and pressures in dynes—volumes in cubic centimeters. The standard pressure of 1 atmosphere (76 cm.) in grams per centimeter is equal to 1033.6 (i.e., 76 times the weight of 1 cc. of mercury at 0° C.) and since the mole occupies 22,400 cc. under standard conditions, (0°, 760 mm.), we have for all gases

$$R=\frac{1033.6\times 22400}{273}=84{,}780 \text{ gram-centimeters,}$$

or, when the pressure is 1 atmosphere, the volume being 22.4 liters

$$R=\frac{1\times 22.4}{273}=0.08204 \text{ liter-atmosphere,}$$

a liter-atmosphere being equal to the work done by the normal atmospheric pressure upon a square decimeter through a decimeter. This unit is an especially valuable one in our later work, so the reader should become familiar with it here.

Finally, expressing p_o in dynes, and $v_{m,o}$ in cubic centimeters, we find

$$R=8.31\times 10^7 \text{ ergs.}$$

These values of R from $\frac{p_o v_{m,o}}{273}$ are of course fundamental in the application of our general equation of state for gases

$$pv_m=RT,$$

and are the only ones which can be found directly from the product of pressure and volume, although we shall find later that R *is also equal to 2 calories*, when the product of pressure and volume are considered as expressed in terms of heat energy, i.e., when the above product in gram-centimeters is divided by the so-called mechanical equivalent of heat (the number of gram centimeters equivalent to 1 calorie). We see from this, then, that R is simply the change in the product pv_m per degree, and so must always be expressed in units which can be employed for such a product.

If the gas is formed from a solid or liquid, i.e., is transformed from a negligibly small volume to the volume it occupies as a gas at p and T, v_m in equation (1) will be the increase in volume, and pv_m (i.e., $p\Delta v_m$) will express the external work done when 1 mole of the gas is formed from negligible volume, against any one, constant, pressure. We shall have then

$$p\Delta v_m = RT,$$

and since, so long as the gas laws hold, pressure and volume at constant temperature will be inversely proportional, RT *will always have the same value for one mole at any one temperature, independent of the pressure, so long as it remains constant. We can always use the* RT *side of the equation, then, to express the work, and need not first find the volume at the required pressure and then their product, for although an infinite number of volumes would be possible, depending on the pressure, the product of* p *and* Δv_m *would always be the same, at the same value of* T*, and equal to* RT. In addition to the definition of molecular or formula weight, as a gas, already given, i.e., the weight occupying the same volume as 32 grams of oxygen, or two grams of hydrogen, under like conditions of pressure and temperature, we have then, the following: *The molecular or formula weight of a substance in the gaseous state is that weight which, in being formed from negligible volume at any temperature* T*, against any constant pressure, does the external work* RT.

Since equation (1) for N moles would lead to NRT, so here the work of forming N moles would naturally be NRT. The units in which it is expressed being dependent upon the one selected for the expression of R (gram-centimeters, calories, liter-atmospheres, ergs, etc.).

In calculating either p, v, or T, when the other two are known, we can make use of equation (1), in the form

$$\frac{p'v'_m}{T'}=\frac{p''v_m''}{T''},$$

where, since we eliminate R, the terms p and v_m can be expressed in any desired units, as their product does not have to give an energy quantity in any definite and recognized units. For this reason in applying the law in this form we can use the pressure in centimeters of mercury if desired, *but only when in this form, in which the R is eliminated; otherwise only the units mentioned above can be applied.*

In place of this relationship, of course, we can also use the simple proportions

$$\begin{aligned} v_1 : v_2 &:: p_2 : p_1 \quad (\text{const. } T)\\ v_1 : v_2 &:: T_1 : T_2 \quad (\text{const. } p)\\ p_1 : p_2 &:: T_1 : T_2 \quad (\text{const. } v). \end{aligned}$$

Changing the volume first, for example, to that at the new pressure, assuming the temperature to remain unchanged; and then changing this to the volume at the new temperature, under the constant pressure. To find the volume of a mole of gas at any temperature and pressure from its value, 22.4 liters at 0° and 76 centimeters, a calculation which we shall often have to make, we find from the above proportions that the most convenient and concise form of expression is:

$$v_{m,t,p}=22.4\times\frac{273+t}{273}\times\frac{76}{p}\text{ liters.}$$

That this form of expression is correct is shown by the fact that by it a higher temperature than 273 would lead to a larger volume; and a pressure smaller than 76 cms. would increase the volume, while one above that value would decrease it.

One thing must be borne in mind always in using this equation to find the actual volume of the mole of gas at any temperature and pressure, viz., that it is only applicable for such cases where the gas can really exist to the pressure p at the temperature in question. Thus we could not find the volume of a mole of water vapor at 25° at any pressure higher than that of the vapor pressure of the water itself at that temperature, viz., 23.76 mm., for a higher pressure than that would cause the vapor to condense to the liquid form. For the vapor of a liquid, thus, the maximum pressure experimentally possible would be the vapor pressure of the liquid at that temperature. We shall return to this in our later consideration of the liquid state itself.

Dalton's law refers to the pressure exerted by the single gases in a mixture of gases.

The pressure exerted upon the walls of a vessel containing a mixture of gases is equal to the sum of the pressures which the single gases would exert were they alone in the vessel. In other words,

$$p = p_1 + p_2 + p_3 + \cdot\ .\ .\ .$$

where p is the total pressure of the system. The exact meaning of this will be seen from the following example: When into a closed exhausted vessel we introduce 1 gram of gas it will exert a certain pressure upon each square centimeter of the surface. If now we introduce a second gram of the same or a different gas, it will exert exactly the same pressure upon the vessel that it would have exerted had the first gram not been there. Upon the walls, however, *with the same gas*, the pressure will be doubled.

One gas law still remains to be considered which has had and still has great value in chemistry; it is *Avogadro's law: All* *gases under the same conditions of pressure and temperature contain in unit volume the same number of moles.* In its original form this relation referred to the hypothetical molecules themselves (not to gram molecules, i.e., moles), and hence was hypothetical. In the form given above, however, it is simply expressive of the definition of molecular weight already given (pp. 3, 8, and 10). As a matter of fact the original form has always been used of late as though it did refer to gram molecules, so that the hypothetical character has been lost, and the relation may well be designated as *Avogadro's law.*

An interesting application of these gas laws has been made by Rebenstorff (Chem. Ztg. **32**, 570, 1908) who measures the volume of a space into which it is undesirable to put a liquid by the measurement of the change in its volume due to a definite change in its pressure. By attaching a water-filled burette (600 cc. capacity) to the enclosed volume, and allowing a portion of the liquid to run out, we decrease the pressure in the tank, which was originally 1 atmosphere, by an amount determinable from the height of water column which has run out of the burette—and at the same time we measure the volume of this, which is the increase in volume due to this decrease in pressure. We have then, if x liters is the increase in volume of an unknown number of liters, and y is the corresponding decrease in pressure, calculated in atmospheres,

$$\text{Orig. Vol.} : \text{Orig. Vol.} + x :: \text{Orig. Press.} - y : \text{Orig. Press.},$$

from which, knowing the original pressure and x and y, we can calculate the original, i.e., the real, volume of the enclosed space in liters.

Variation from the gas laws. The equation of Van der Waals.—While the law of Boyle-Mariotte, as to the constancy of the product of pressure and volume at constant temperature, is purely an ideal law, showing variations when applied to any one definite gas, the variations in general, especially in the case of the so-called permanent, i.e., not readily liquefiable, gases, *are almost negligible up to pressures of three atmospheres; and the higher the temperature of the gas, the smaller is the observed error, and the wider the range through which the law holds.* In the table below are given the pressures which are necessary, in the cases of air, CO_2, N and H, to reduce the volume of the gases to an even fraction of the original, unit, volume, and which, if the law held, should be inversely proportional to them. Here the difference between the behavior of the more permanent gases and that of the easily liquefiable CO_2 is to be noted; for in the latter case the pressures are not only smaller than those calculated from the law of the inverse ratio of pressure and volume, but are also much less than those necessary in the case of either air or nitrogen. The behavior of hydrogen is also striking here, for the pressure necessary, and in that it differs from all other gases, is always *larger* than that which would be calculated from the law.

COMPRESSIBILITY OF GASES (CONSTANT TEMPERATURE).

Vol.	Air.		CO_2.		N.		H.	
	Pressure Meters Hg.	Δ	Pressure Meters Hg.	Δ	Pressure Meters Hg.	Δ	Pressure Meters Hg.	Δ
1	1.0000	+0.0000	1.0000	+0.0000	1.0000	+0.0000	1.0000	−0.0000
$\frac{1}{2}$	1.9978	+0.0022	1.9829	+0.0171	1.9986	+0.0014	2.0011	−0.0011
$\frac{1}{4}$	3.9874	+0.0126	3.8973	+0.1026	3.9919	+0.0081	4.0068	−0.0068
$\frac{1}{8}$	7.9456	+0.0543	7.5193	+0.4807	7.9641	+0.0359	8.0339	−0.0339
$\frac{1}{10}$	9.9162	+0.0838	9.2262	+0.7738	9.9435	+0.0560	10.0560	−0.0560
$\frac{1}{12}$	11.8823	+0.1177	0.8632	+1.1368	11.9191	+0.0809	12.0844	−0.0844
$\frac{1}{16}$	15.8044	+0.1956	13.9260	+2.0740	15.8597	+0.1403	16.1616	−0.1616
$\frac{1}{20}$	19.7198	+0.2801	16.7054	+3.2946	19.7885	+0.2115	20.2687	−0.2867

At a pressure of about 20 meters of mercury it will be observed from the Table, the law fails to hold by about 1.5% for the so-called permanent gases, and by about 25% for the more readily liquefiable one, CO_2, which, however, is above its liquefying temperature here.

In the following table are grouped together the experimental values of the term *pv* for various gases up to a high pressure. Ethylene in this case is at a temperature of 20°, i.e., above its liquefying temperature, 9° C., where a pressure of 58 atmospheres produces the liquid phase. The weight of gas taken here is that which occupied the volume of the apparatus at 0° and atmospheric pressure, so the figures are only relative.

VALUES OF *pv* FOR VARIOUS GASES (CONSTANT TEMPERATURE)

P (meters of Hg).	*pv* for				
	Air.	O.	H.	CO.	Ethylene.
24.1	26968	26843	27381	27147	21473
34.9	26908	26614	27618	27102	18352
45.2	26791	—	27652	27007	12263
55.5	26789	26185	27960	27025	9772
64.0	26778	26050	28129	27060	9370
72.2	26792	25858	28323	27071	9703
84.2	26840	25745	28533	27158	10675
101.5	27041	25639	—	27420	12210
133.9	27608	25671	29804	28092	15116
177.6	28540	25891	30755	29217	18962
214.5	29585	26536	31625	30467	22115
250.2	30572	—	32426	31722	25065
303.0	—	28756	—	—	29333
304.0	32488	—	33887	33919	—

Here it is to be noted that while the value of *pv* increases continually for hydrogen, it first decreases to a minimum, in the case of the other gases, and then increases with increased pressure, just as it does for hydrogen at all pressures. The minimum for ethylene, a readily liquefiable gas at lower temperatures, as will be seen, is at 64 meters pressure, but one-third of what it is at 304 meters, and less than one-half what it is at 24.1 meters.

The peculiar behavior of hydrogen as compared with the other gases was first observed by Natterer and ascribed by Budde to the fact that the hypothetical molecules themselves occupy a volume, and hence their volume should be subtracted from the observed volume to give the true volume of the gas which is really subject to compression. Whatever the explanation, the equation suggested by Budde, viz.,

$$p(v-b) = \text{constant},$$

(where b and "constant" are specific values for the gas and constant for it at all pressures) would seem to hold rigidly at pressures of from 2800 to 1000 meters of mercury, at any rate, as will be seen from the table below.

HYDROGEN

$p(v-b) = constant$

p (meters of Hg).	$\frac{1}{v}$	b	p (meters of Hg).	$\frac{1}{v}$	b
2790	1008	0.00083	1434	758	0.00081
2689	998	0.00083	1326	728	0.00082
2594	988	0.00082	1226	698	0.00081
2505	978	0.00082	1104	658	0.00081
2423	968	0.00082	1015	628	0.00080
2374	958	0.00081	903	588	0.00078
2213	938	0.00081	824	558	0.00076
2098	918	0.00081	706	508	0.00073
1995	898	0.00081	608	458	0.00071
1904	878	0.00081	505	398	0.00070
1821	858	0.00081	408	338	0.00067
1701	828	0.00081	300	258	0.00072
1623	808	0.00082	209	188	0.00071
1508	778	0.00082			

Here, of course, the weight of gas in all cases is the same, and is that which occupied the unit volume $\left(\frac{1}{v}=1\right)$ at 1 meter pressure, the v being used to distinguish it from the volume of 1 gram, viz, v_s.

Although this new form of equation seems to give correct values for hydrogen under very high pressures, it, of course, cannot be employed for other gases; for with them there must be some other factor as well to be considered, so as to provide for the minimum value of pv they exhibit, but which does not exist in the case of hydrogen.

Regnault found that his measurements of the compressibility of gases could be accurately expressed by the empirical equation

$$pv = 1 - A\left(\frac{1}{v} - 1\right) + B\left(\frac{1}{v} - 1\right)^2,$$

where A and B are constants; for hydrogen the constant A being negative in sign.

In 1873 Van der Waals derived the equation

$$\left(p + \frac{a}{v^2}\right)(v - b) = \text{constant},$$

and showed that it represented exceedingly well in general the behavior of a gas under high pressures. Here a is considered as the cohesion pressure existent in the gas itself, which is the greater, the smaller the volume, and b is considered as four times the volume occupied by the hypothetical molecules themselves. Whatever meaning is ascribed to a and b, however, it will be seen that they are terms which must be evaluated by experiment for each gas, so that the equation, in so far as its application is concerned, is similar to the empirical one of Regnault's, where there are also two unknown constants, A and B, for each gas, which can only be given numerical values by aid of experiment.

Writing Van der Waals' equation in the form

$$pv = \text{constant} - \frac{a}{v} + \frac{ab}{v^2} + bp,$$

we see that when v is large and p is small, $\frac{ab}{v^2}$ and bp disappear as compared to $\frac{a}{v}$; and that when $\frac{a}{v}$ is most nearly equal to $\frac{ab}{v^2} + bp$, we have the smallest variation from the Boyle-Mariotte law, according to which pv should be equal to a constant.

In the table below, this law is applied to the results on the compressibility of nitrogen at a constant temperature of 22°. Here the constants a and b are calculated from Regnault's constants A and B as found by him for pressures up to 20 meters of mercury only, so the table involves an extrapolation which probably accounts for some of the variations observed. To get a and b here we rewrite Van der Waals' equation in the form

$$pv = \text{constant} - \frac{a - b\,(\text{constant})}{v} + \frac{ab}{v^2},$$

i.e., on the assumption that the term p in bp can be expressed, as it would be by aid of the Boyle-Mariotte law, by $\frac{\text{constant}}{v}$. This also introduces a slight error in the table of course.

It is to be remembered in all cases here that v *is not the* v_s *we used in discussing the simpler gas law, i.e., the volume occupied by 1 gram of gas, but is the volume produced at the pressure and temperature in question from that weight of gas which at 0° and 1 atmosphere pressure occupied 1 liter.* Writing the Van der Waals' equation in its complete form, then, we would expect to have

$$\left(p + \frac{a}{v^2}\right)(v - b) = \frac{\text{constant}}{273} \times T, \quad \left(\frac{\text{constant}}{273} = \frac{\left(1 + a\right)(1 - b)}{273}\right),$$

or, for the molecular amount of gas (which would be 22.4 times the weight of what was 1 liter at $T=273°$ and 1 atmosphere pressure)

$$22.4\left(p+\frac{a}{v^2}\right)(v-b)=RT, \left(R=\frac{22.4\left(1+a\right)(1-b)}{273}\right),$$

where R, if p is in atmospheres, should have the value of approximately 0.08204 liter atmosphere, since a and b are small as compared to 1.

In column 1 of the table is given the observed pressure, in 2 the observed volume (which was unity, 1 liter, at 0° and 1 atmosphere pressure); in 3 is the product of columns 1 and 2. In column 4 is the product pv as calculated from the complete Van der Waals' equation above, in the form

$$pv=1.080-\frac{a}{v}+\frac{ab}{v^2}+bp,$$

where $a=0.002303$ and $b=0.001767$, and 1.080 $\left(=\frac{\text{constant}}{273}\times T\right)$ is found from the original conditions of a liter at 1 atmosphere and 273°, i.e.,

$$\frac{\text{constant}}{273}=\frac{(1+0.002303)(1-0.001767)}{273}, \text{ and } \frac{\text{constant}}{273}\times 295=$$

1.080. In 5 is the value of the correction term for pressure, $\frac{a}{v^2}$; in 6 the total pressure, $p+\frac{a}{v^2}$; in 7 is the corrected volume, $v-b$; in 8 is the value found for $\left(p+\frac{a}{v^2}\right)(v-b)$; and, finally, in 9 is this value after multiplication by $\frac{22.4}{295}$. Here R should equal, if the law is perfectly rigid in holding, $\frac{1.080 \times 22.4}{295} = 0.0820$, which corresponds to the value .08204 we have been using with the Boyle-Mariotte-Charles law.

NITROGEN AT 22° C.

$a = 0.002303$; $b = 0.001767$

p (atmos.)	v (liters).	pv (obs.).	pv (calc.).	$\frac{a}{v^2}$	$p + \frac{a}{v^2}$	$v - b$.	$\left(p + \frac{a}{v^2}\right) \times (v - b)$.	R.
27.29	0.03916	1.069	1.072	1.50	28.79	0.03739	1.076	0.0817
62.03	0.01716	1.064	1.069	7.82	69.85	0.01539	1.075	0.0816
90.98	0.01173	1.068	1.074	16.72	107 70	0.00996	1.073	0.0815
126.9	0.00852	1.081	1.090	31.74	158.64	0.00675	1.071	0.0813
168.8	0.00657	1.109	1.122	53.37	222.18	0.00480	1.067	0.0810
208.6	0.00546	1.139	1.163	77.36	286.00	0.00369	1.055	0.0801
290.9	0.00416	1.211	1.275	132.90	423.80	0.00240	1.015	0.0771

As will be observed from this table the law of Van der Waals holds exceedingly well, considering that the values of a and b were found from results going only as high in pressure as 20 meters of mercury, and even then were calculated by aid of a simplifying assumption that must in itself introduce some error. Up to 168 atmospheres as will be noted the error is only a few tenths of 1%, and at 290.9 atmospheres is only 6.0%, where the error according to the Boyle-Mariotte-Charles law is about 15%.

A better illustration of the holding of Van der Waals' law, and a more searching test of it, is given by its application to ethylene, the gas which shows such a distinct and striking minimum value of the experimental product pv. Here the values of a and b are calculated, not as above from the actual behavior of the gas, but from its critical constants (see Liquids).

In the table below, arranged just as was that referring to nitrogen, these results are presented.

ETHYLENE AT 20°

$a=0.00786$; $b=0.00224$.

p (atm.).	v (liters).	pv (obs.).	pv (calc.).	$\frac{a}{v^2}$	$p+\frac{a}{v^2}$	$v-b$	$(p+\frac{a}{v})$ $\times(v-b)$.	R.
31.58	0.02894	0.914	0.904	9.39	40.97	0.02670	1.094	0.0836
45.80	0.01705	0.781	0.786	27.03	72.83	0.01481	1.078	0.0824
72.86	0.00571	0.416	0.409	241.1	313.96	0.00347	1.089	0.0833
84.16	0.00474	0.399	0.398	349.6	433.76	0.00250	1.084	0.0829
94.53	0.00437	0.413	0.419	411.5	506.03	0.00213	1.077	0.0823
110.47	0.00411	0.454	0.459	465.4	575.87	0.00187	1.076	0.0823
133.26	0.00390	0.520	0.526	516.6	649.86	0.00166	1.078	0.0823
176.01	0.00365	0.643	0.647	588.8	764.81	0.00141	1.081	0.0826
233.58	0.00345	0.807	0.808	658.6	892.18	0.00121	1.083	0.0828
282.21	0.00334	0.941	0.943	706.6	988.81	0.00110	1.083	0.0828
321.14	0.00324	1.067	1.072	747.1	1076.24	0.00100	1.079	0.0825
398.71	0.00313	1.248	1.264	802.4	1201.10	0.00089	1.069	0.0817

For ethylene the constant used in calculating is 1.0840, and is found as in the case of nitrogen from the original volume and pressure at 273°. We have here

$$\frac{(1+0.00786)(1-0.00224)}{273}=\text{constant},$$

and constant $\times 293=1.0840$.

It must be conceded here that the agreement between the results of the equation and those from experiment is very remarkable, the largest difference being but 1.5% at 398.7 atmospheres; even though the term pv passes through such a marked minimum value.

Some of the known a and b values are given below; for hydrogen a is usually considered as being nearly zero, since the value of pv of this gas does not pass through a minimum, and that is produced, as can be seen from the equation, by a comparatively large value of a, with a small value for b. *b in all cases experimentally is the volume in liters which must always be subtracted from the then volume of what was 1 liter at 0° and 1 atmosphere pressure, to give the really compressible volume of the gas.*

VALUES OF VAN DER WAALS' CONSTANTS, a AND b

	a	b
Carbon dioxide	0.00874	0.0023
Sulphur dioxide	0.039	—
Air	0.0037	0.00260
Hydrogen	0.000	0.00673*
Ethylene	0.00786	0.00224
Nitrogen	0.00303	0.002325

The term b, in general, is observed to decrease with increased temperature, i.e., the higher the temperature, the more nearly does the ideal Boyle-Mariotte-Charles law hold.

With respect to the law of Charles as to the extent of the expansion per degree at constant pressure, or the increase in pressure per degree at constant volume, it may be said that that also is an ideal law when considered alone. In the following table are given some of the values of the changes due to heating a gas 1°, which of course should be equal to $\frac{1}{273}=0.00367$, if Charles' law held rigidly; i.e., $p_t=p_o\left(1+\frac{1}{273}t\right)$ for constant volume, or $v_t=v_o\left(1+\frac{1}{273}t\right)$ for constant pressure.

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* The value in the previous table referred to the correction necessary in the unit volume when the pressure is in meters of mercury. Here all figures refer to what was originally the unit volume in liters at 0° and 1 atmosphere pressure. In connection with the constant b, of the Van der Waals' equation and the compressibility of a gas, see the recent paper by T. W. Richards, J. Am. Chem. Soc., **36**, 617, 1914.

OXYGEN

Increase in Pressure per Degree at Constant Volume.		Increase in Volume per Degree at Constant Pressure.	
Pressure.	Change.	Pressure	Change.
180–230 mm.	0.003665	100 atmos.	0.00486
354 "	0.003670	200 "	0.00534
583 "	0.003669	400 "	0.00459
1 atmos.	0.003674	600 "	0.00357
		800 "	0.00288
		1000 "	0.00241

NITROGEN.

200–230 mm.	0.0036643	200 atmos.	0.00434
1 atmos.	0.0036682	400 "	0.00359
		600 "	0.00282
		800 "	0.00240
		1000 "	0.00218

HYDROGEN.

0.25 mm.	0.003623	200 atmos.	0.00332
700 "	0.003663	400 "	0.00295
760 "	0.003668	600 "	0.00261
1000 "	0.003663	800 "	0.00241
		1000 "	0.00218

AIR

760 mm.	0.003665	760 mm.	0.003671
1001 "	0.003674	1001 "	0.003673
2000 "	0.003690	2620 "	0.003696
20000 "	0.003887		
100000 "	0.004100		

At low pressures here (i.e., below 3 atmos.) it would seem that the difference between the results of the law of Charles and those of experiment is negligible; but that at high pressures the change per degree in the volume at constant pressure decreases with increased pressure; in other words, the change in volume due to an increase of 1° in temperature is less at high pressures than at low.

The specific gravity of gases.—The specific gravity of a gas is the weight of the unit of volume, but as this is always very small it is customary to find in these terms the value for a certain gas to be used as a standard, and then to express the density of other gases in terms of the density of this gas, taken as unity.

We see from this that as far as concerns gases, we have two kinds of specific gravity or density. One of these gives us actually the weight in grams of 1 cc. of the substance at T and p, since it is based upon unit volume (1 cc.) of water at 4°, and that by definition is the weight of 1 gram. The second form, on the other hand, gives us simply the relative weight of 1 cc. of the gas at T and p, in terms of the weight of 1 cc. of the standard gas, at the same T and p, taken as unity. Let us designate the value based upon 1 cc. of water at 4° by d, and that based upon 1 cc. of another gas at the same pressure and temperature by δ, using a sub letter to show what the standard gas is. Thus d actually represents the weight in grams of 1 cc. of the gas under the existing conditions, while δ simply gives us the ratio of the weights of equal volumes of the two gases, *both under identical conditions of temperature and pressure.*

As the composition of air varies, oxygen has been chosen as the chemical standard for the calculation of δ. Since this is very easily obtained in the pure state and its combining weight with other elements can be accurately determined, its advantages as a standard are apparent.

One liter of O weighs 1.4292 grams at 0° and 76 centimeters pressure. Its specific volume, i.e., the volume of 1 gram at any temperature and pressure, then, is

$$v_s = \frac{1}{0.001429} \cdot \frac{76}{p} \cdot \frac{T}{273} = 699.8 \frac{76T}{273p} \text{cc.}$$

Its specific gravity or density, *d*, i.e., the weight in grams of 1 cc., at any temperature and pressure, is then the reciprocal of the specific volume, i.e.,

$$d = \frac{1}{v_s} = 0.001429 \cdot \frac{273p}{76T} \text{ grams.}$$

The volume of 1 molecular weight of oxygen, i.e., 32 grams, the basis of our molecular weight system, thus becomes at any temperature *T* and any pressure *p*,

$$Mv_s = v_m = 32 \times 0.6998 \frac{76T}{273p} = 22.4 \frac{76T}{273p} \text{ liters.}$$

Since the molecular weight of a gas is that weight which occupies the same volume under like conditions of *T* and *p* as the molecular weight in grams of any other gas, or of 32 grams of oxygen, we can calculate the molecular weight, from the known weight of a definite volume, by aid of either of the following relationships:

$$M : 22.4 \frac{76T}{273p} :: 1 : \text{vol. in liters at } T \text{ and } p \text{ of 1 gram of the gas,}$$

or

$$M : 22.4 \frac{76T}{273p} :: \text{wgt. of 1 liter at } T \text{ and } p : 1.$$

As the molecular weights of all gases must occupy the same volume under identical conditions of *T* and *p*, it is plain that the weights of 1 cc. of these gases, i.e., the weight of the same fraction of the total volume in all cases, must be related as the molecular weights themselves; for multiplication of those weights by the same factor would give the molecular weights of the gases.

We have then

$$M_1 : M_2 :: \text{wgt. 1 cc. of gas (1)} : \text{wgt. 1 cc. of gas (2)},$$

both at the same T and p; or, using oxygen as the standard, the molecular weight of any gas is

$$M = 32 \frac{\text{wgt. 1 cc. of gas at } T \text{ and } p}{\text{wgt. of 1 cc. of oxygen at } T \text{ and } p}.$$

But this ratio of the weights of equal volumes is what we have designated above as δ; in other words, is the weight of one gas in terms of the weight of the other taken as unity, both under the same conditions of T and p.

We have then for the molecular weight of any gas, taking oxygen as the standard,

$$M = 32\,\delta_o,$$

i.e., *the molecular weight of any gas is 32 times its density referred to oxygen. Or, in general, the molecular weight of any gas is equal to the product of its density referred to a standard gas, into the molecular weight of the standard gas.*

Thus the molecular weight of any gas is twice its density referred to hydrogen; thirty-two times its density referred to oxygen, and twenty-eight times its density referred to nitrogen, or two hundred times its density referred to gaseous mercury; for 2, 32, 28 and 200 are the molecular weights of H, O, N and Hg.

In case the density of the gas is known only in terms of the density of air taken as unity, we find

$$M = 28.95\ \delta_{\text{air}},$$

for since 1 cc. of air under standard conditions weighs 0.0012932, as compared to 0.0014292 for oxygen, $32\delta_o$ becomes

$$32 \times \frac{\delta_{\text{air}}}{\frac{0.0014292}{.0012932}} = 28.95\,\delta_{\text{air}} = M.$$

The density, and consequently the molecular weight, of a gas can also be found indirectly without the use of weights. This method depends upon the relation of the velocity of outflow of a gas through a small aperture to the specific gravity of the gas. The formula is derived as follows: Let p be the difference between the pressure under which a gas exists and that of the atmosphere, and v be the volume of the gas which flows out in the unit of time. The total work done by the change in volume is then pv. Since this work is used to force the gas out, it is equal to the increase of kinetic energy of the gas, i.e.,

$$pv = 1/2mu^2,$$

where u is the velocity of outflow of the gas, and m is its mass. If equal volumes of different gases are considered, flowing through the same-sized openings under the same pressure, then,

$$pv = 1/2m_1u_1^2, \quad \text{and} \quad pv = 1/2m_2u_2^2,$$

i.e.,

$$u_1 : u_2 :: \sqrt{m_2} : \sqrt{m_1},$$

or, since the masses of equal volumes are proportional to their densities,

$$u_1 : u_2 :: \sqrt{d_2} : \sqrt{d_1}.$$

The apparatus used by Bunsen is very simple. A glass tube having a very fine opening at one end, below which is a stop-cock, is clamped into a vessel of mercury. In this tube is a piece of glass rod to act as a float, while on the outside there are two marks close together. The gas is now passed into the tube at a certain pressure, and the tube lowered into the mercury until the float is just at the lower mark. The cock is then opened and the time necessary for the passage of the float from the lower to the upper mark observed. Since the time of outflow is inversely proportional to the velocity, for the same volume, we have

$$t_2 : t_1 :: \sqrt{d_2} : \sqrt{d_1}.$$

By carrying out the experiment for one gas and then for oxygen, both at the same pressure, we can find the density of the gas in terms of oxygen. The results by this method, and this is true in a lesser degree for all methods for molecular weight, are not exact,* but are simply intended to indicate what number of combining weights of an element, or what weight of a compound, represents the formula weight. For this reason very great accuracy is not necessary, for it is only a question of finding whether the combining weight, or the simplest ratio, as found by analysis, is to be multiplied by the factor 1, 2, 3, etc.

Abnormal vapor densities. Dissociation.—The specific gravity or density of the gases generated by heat from substances is found in many cases to be too small to correspond to the accepted formulas, i.e., the molecular weights thus determined are smaller than the generally accepted values. And, further, the molecular weight is found to vary with the temperature, pressure, and some other factors. These results, the densities, naturally, must be obtained for this purpose with greater accuracy than those mentioned above if the process is to be followed at all closely. Since, according to our definition of molecular weight, 1 mole occupies 22.4 liters at 0° and 760 mm. pressure,

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* For a precision method for the determination of a gaseous density, see Schulze, Physik Zeitsch. 14, 922, 1913.

(or $22.4\frac{76T}{273p}$ liters at T and p_1), a smaller density would represent a decomposition of the substance employed. Thus if a substance decomposes in such a way that from each mole of the gas there are two others formed, the vapor density of the system must be one-half what it should be: for each mole or volume of the original gas which is decomposed gives rise to two moles or volumes of the constituent gases, at the same temperature. These two moles, or volumes, however, will weigh the same as the original one mole or one volume, so that the weight of one volume of the mixed gases will be one-half that of one volume of the undecomposed gas. St. Clair Deville called this decomposition *dissociation.* Thus solid NH_4Cl first gasifies and then dissociates according to the scheme

$$NH_4Cl \rightleftarrows NH_3 + HCl,$$

where the sign $\rightleftarrows$ means that the reaction may go in either direction, according to the conditions. That these two gases, NH_3 and HCl, are actually present in the system, as well as undissociated, gaseous, NH_4Cl, can be shown in the following way (Pebal and Than): A lump of solid NH_4Cl is placed in a tube upon an asbestos plug, and the temperature of the tube raised. The NH_4Cl now volatilizes and dissociates in NH_3 and HCl. Since NH_3 is the lighter gas (*and the speeds of diffusion of gases, under the same pressure, are inversely proportional to the square roots of their densities or molecular weights, page 27*), it diffuses more rapidly through the asbestos plug than the HCl; consequently on one side of the plug we shall have an excess of HCl, and on the other an excess of NH_3. The presence of these two products separated thus by the diffusion may be shown by passing a current of dry air through the parts of the tube on each side of the plug and then over moistened litmus paper, which will show the nature of the gases present, i.e., acid on one side and alkaline on the other.*

Since the density of the substance, in case of a dissociation, decreases to an extent dependent upon the temperature, it is an important thing to be able to find the degree of the dissociation at any one temperature, i.e., to determine the extent of the reaction (p. 29) forming the products on the right.

This can be found from the relation of the vapor density to the dissociation, i.e., from the dependence of both upon the number of moles. If, for example, α is the percentage of the gas dissociated, i.e., *the degree of dissociation*, and we start with 1 mole of the gas, then $1-\alpha$ is the undissociated portion. If there are i moles of the products formed from 1 mole of the gas, i.e., two in the above case, the total number of moles present at any time is

$$(1-\alpha)+i\alpha, \text{ or } 1+(i-1)\alpha.$$

The ratio, then, of 1 to $1+(i-1)\alpha$ will be the same as that of the vapor density as it is, to the vapor density as it should be, both based upon the same standard gas, naturally, i.e.,

$$1 : 1+(i-1)\alpha :: \delta_d : \delta_u.$$

Here δ_u is the vapor density as it should be (i.e., as it is without dissociation), and δ_d is what it actually is, for it is clear that, since, under constant pressure, the volume is proportional to the number of moles

$$1 : 1+(i-1)\alpha :: v_u : v_d$$

and

$$v_u : v_d :: \delta_d : \delta_u,$$

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* This dissociation is found by Baker (Trans. Chem. Soc. 65, 611, 1894, and 73, 422, 1898) to take place only when moisture is present. See also Abegg and Johnson, Zeit. f. phys. Chem., 61, 455–463, 1908, and Smith and Menzies, Jour. Am. Chem. Soc., 32, 1458, 1910.

for the same total weight of gas is now contained in a larger volume, so that the actual or relative weight per cc. has decreased.

The degree of dissociation, then, is

$$\alpha=\frac{\delta_u-\delta_d}{(i-1)\,\delta_d}.$$

If a substance dissociates completely into two products, its vapor density is 1/2 what it should be; if into three, 1/3; as can be shown by substituting 1 for α, and 2 for i when two products are formed from one, for then we would have 1+1 moles produced from 1 original one; and when three moles of product are produced ($i=3$) we would have 1+2, etc.

Thus the density of ammonium chloride at a certain temperature is found to be nearly 1/2 what it should be; hence

$$NH_4Cl \rightleftarrows NH_3+HCl.$$

And the density of ammonium carbamate at a high enough temperature is found to be nearly 1/3; hence

$$NH_2CO_2NH_4 \rightleftarrows CO_2+2NH_3.$$

It will be seen from the above that the process of dissociation, since it decreases the density of the system, produces a *smaller average* molecular weight of the dissociating system, than that possessed by the substance with which we start. So that in the above case the molecular weights calculated from complete dissociation would give one-half the value corresponding to NH_4Cl and one-third the value corresponding to $NH_2CO_2NH_4$. Or the value at any intermediate value would be,

$$\text{Av. } M=\frac{M}{(1-\alpha+i\alpha)}.$$

Since when 1 mole of gas is formed from a solid or liquid against any constant pressure, the external work done at T, by definition, is RT; the work when $(1-\alpha+i\alpha)$ moles are given off must be $(1-\alpha+i\alpha)RT$.

The process of dissociation is a very common one, and proofs of it, quite as good as the one by Pebal and Than already mentioned, are numerous. A few of them are given briefly below.

PCl_5 when heated shows the green color of chlorine gas which increases with the temperature. This is due to the dissociation into PCl_3 and Cl_2, which, as with all gaseous dissociation phenomena, *increases with the temperature.*

N_2O_4 by heat becomes brownish red, due to the formation of $2NO_2$. At 500° C. this color disappears entirely, for then $2NO_2$ breaks down into $2NO$ and O_2, both of which are colorless.

When a gas composed of a heavy metallic and a light gaseous element is dissociated by heat in an open tube, and cooled suddenly, the heavy element will crystallize out. This is due to the fact that the two gases go through the tube with a different velocity (which is inversely proportional, under any one pressure, to the square root of the density or molecular weight of the gas), so that when suddenly cooled, the compound forms until all the lighter gas remaining is used up, when the excess of the more slowly moving one separates out on the walls in the metallic state. An example of this is given by Marsh's test for arsenic.

The specific heat of a dissociating gas is very large owing to the fact that the heat supplied increases the dissociation as well as the temperature. When the dissociation is complete, however, the specific heat becomes constant. Thus we have for acetic acid gas:

t..................	129°	160°	200°	240°	280°
Sp. ht..............	1.50	1.27	0.95	0.64	0.480

The extent to which the dissociation of a gas takes place, i.e., the value of α, is dependent upon the two conditions, *temperature* and *pressure.*

The higher the temperature, the greater the dissociation (up to $\alpha = 1$); and, consequently, the lower the temperature the smaller will be the dissociation, i.e., the larger, and more nearly normal will be the molecular weight of the system.

When the dissociation is accompanied by an increase in the volume of the system, we find that *the higher the external pressure to which we subject the system, the smaller will be the extent of the dissociation.* This fact can be foreseen by aid of a very general theorem advanced by Le Chatelier, viz.: *any change in the factors of equilibrium from the exterior causes the system to react in the direction favored by the change.* Thus, increased external pressure would favor the equilibrium reacting in such a way as to decrease its volume, i.e., would cause the undissociated product (the one of smaller volume) to be formed. It is clear from this principle, then, that increased external pressure should decrease the degree of dissociation, while decreased pressure should increase it.

This reaction due to a change in pressure is general for all reactions of the type $PCl_5 \rightleftarrows PCl_3 + Cl_2$, or $2NO_2 \rightleftarrows 2NO + O_2$; but, naturally is not observed in systems of the type $2HI = H_2 + I_2$, for here as we have the same number of moles on the two sides, the volume remains constant as the reaction progresses. A change in pressure, then, would not affect either side more than the other, and therefore the degree of dissociation must be independent of the magnitude of the external pressure—as indeed experiment shows it to be.

We can also *decrease the extent of the dissociation of a system,* or indeed of any reversible chemical reaction, *by previously, or at any other time, introducing into the system one of the products produced by the reaction.* Thus PCl_5 dissociates to a lesser degree, in the presence of either chlorine or phosphorus trichloride, than it does under ordinary conditions. And if a sufficient excess of the product be present the dissociation can practically be prevented entirely.

The effect of these three factors, discussed above, viz., temperature, pressure and the presence of a product of the reaction coming from another source, can all be calculated quantitatively and accurately by a law we shall derive later—*the law of mass action;* for the present, however, we shall only use them as principles which enable us to follow qualitatively the behavior of chemical systems under varying conditions.

In considering systems of gases in this way we must distinguish clearly between those in which a solid is dissociating into gases, and yet cannot exist as a gas itself; and those where the solid itself forms a gas, which then dissociates. An example of the former is the case of solid NH_4HS, and of the latter is solid NH_4Cl. In systems of the former type, increased pressure simply causes a decrease in the amount of the gaseous products, and an increase in the solid, but the dissociation itself must still be considered as equal to 100%, for nothing else but the products are there in the gaseous state. Increased pressure when applied to systems of the second type, on the other hand, actually causes a change in the *relative* amounts of the gases present, i.e., decreases that of the products, and increases that of the undissociated gas.

If, for example, we have equivalent amounts of two gases produced from a solid, which does not itself exist as a gas, a change in pressure on the system can only change the *absolute* amounts of the gases present; *relatively*, they remain the same, however, for we still have such an amount of each which corresponds to one-half the total pressure of the system, in the case of $NH_4HS \leftrightarrows H_2S + NH_3$, for example.

In the gas from a solid which exists as a gas itself, and then dissociates, for example to 50% into two products in equivalent amounts, we would have of each of the three constituents, under normal conditions, an amount corresponding to $\frac{.5}{1.5}$, i.e., one-third, of the total pressure of the system. An increase of pressure here, which drives back the dissociation to 25%; would then change not only the *absolute*, but also the *relative* amounts of the three gases, for now we would not have $\frac{.5}{1.5}$ of each, but $\frac{.75}{1.25}$ of the undissociated gas, and $\frac{.25}{1.25}$ of each of the two gaseous constituents, and the pressure of each of the constituents will now be one-fifth of the total pressure instead of one-third, and that of the undissociated gas will be three-fifths of the total pressure, in place of one-third.

The following tables will serve to show how great the effect of temperature and pressure is upon the dissociation of a gaseous substance:

DISSOCIATION OF NITROGEN TETROXIDE, N_2O_4

Atmospheric Pressure

δ_{air} of $N_2O_4 = 3.18$; of $NO_2 + NO_2 = 1.59$

Temp. (t)	δ_{air}.	Percentage Dissociation.
26°.7	2.65	19.96
35°.4	2.53	25.65
39°.8	2.46	29.23
49°.6	2.27	40.04
60°.2	2.08	52.84
70°.0	1.92	65.57
80°.6	1.80	76.61
90°.0	1.72	84.83
100°.1	1.68	89.23
111°.3	1.65	92.67
121°.5	1.62	96.23
135°.0	1.60	98.69
154°.0	1.58	100.00

DISSOCIATION OF PCl_5

Atmospheric Pressure

δ_{air} of $PCl_5 = 7.2$; $PCl_5 + Cl_2 = 3.6$

Temp. (t)	δ_{air}.	Percentage. Dissociation.
182°	5.08	41.7
190°	4.99	44.3
200°	4.85	48.5
230°	4.30	67.4
250°	4.00	80.0
274°	3.84	87.5
288°	3.67	96.2
300°	3.65	97.3

DISSOCIATION OF H_2O VAPOR AND CO_2

Atmospheric Pressure

$2H_2O \rightleftarrows 2H_2 + O_2$.		$2CO_2 \rightleftarrows 2CO + O_2$.	
T.	100α.	T.	100α.
1300	0.0029	1300	0.0041
1500	0.0221	1395	0.0142
1705	0.108	1443	0.025
2155	1.18	1478	0.029
2300	2.6	1498	0.047
2642	4.3	1565	0.064
2761	8.6	2640	21.0
2834	9.8	2900	49.2
2929	11.1	3116	76.1

DISSOCIATION OF N_2O_4

Equal Temperatures Varying Pressures

Temp. (t)	Pressure.	δ_{air}.	Percentage Dissociation.
18°.0	279 mm.	2.71	17.3
18°.5	136 "	2.45	29.8
20°.0	301 "	2.70	17.8
20°.8	153.5 "	2.46	29.3

The molecular weights (see definition, pp. 3 and 10) of some of the elements in the gaseous state are given below and will serve to show the importance of the process of dissociation, and how dependent the molecular weight is upon the temperature.

ARSENIC

t° C.	M.	
644	309	$As_4 = 300$
670	308	$As_2 = 150$
1715	157	
1736	160	

PHOSPHORUS

t° C.	M.	
313	128	$P_4 = 124$
500	126.1	$P_2 = 62$
1484	105	
1678	93·3	
1708	91	

IODINE

t° C.	M.	
253	285	$I_2 = 253.8$
1330	162	$I = 126.9$

We see from these that the higher the temperature the simpler becomes the formula. Iodine at high temperatures is monatomic, as are mercury between 446°–1731°, cadmium at 1040°, tin at 1400°, sodium and potassium and silver; and sulphur in the gaseous state, according to the temperature, may be S_8, S_6, S_4, or S_2, the latter being the condition at 800° and above.* Mixtures of these four forms of sulphur can also exist, at the lower temperatures, the average molecular weight of the systems lying between the two extremes, S_8 and S_2. At higher temperatures, 1900–2000° C., the S_2 is observed to break down further, to the extent of 50%, into the form of $2S$ (Nernst),† although Biltz and Meyer found the formula weight to be 63.5 at 1719° C.

Among compounds we find the chlorides of iron and aluminium, Fe_2Cl_6 and Al_2Cl_6, only to exist at comparatively low temperatures, being present in the forms $FeCl_3$ and $AlCl_3$ at higher ones.

In the case of a few gases we find that *the substance, in place of dissociating, seems to associate*, i.e., the molecular weight of the vapor is not only larger at low temperatures than at high, but is also larger than it should be according to the generally accepted chemical formula; to which, however, it approaches at the higher temperatures. Increased pressure here also causes the associated state to persist, i.e., the higher the pressure, the greater, within certain limits, is the molecular weight. A typical example of such a behavior is observed with the vapor of acetic acid, and there may also be other substances which show this peculiarity.

Volume, partial pressure and concentration.—For the complete description of a gaseous system composed either of a single gas or a mixture of gases it is essential that we have a convenient method of representing the amount of gas present. Thus far, for this purpose, we have used either the density of the gas or the volume (v_m) which contains 1 mole, but these are not the only forms possible, nor are they always the most convenient. The other two forms possible are *concentration*, i.e., *the number of moles per liter* (c), *and partial pressure* (p), i.e., *the pressure*

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* See Preuner and Schupp. Zt. f. phys. Chem. 68, 148, 1909.

† See Zt. f. Elektrochem., 9, 627, 1903.

that would be exerted at the temperature in question if the constituent gas alone occupied the volume of the system.

The relationship existing between v_m, p, and c is shown by the following, almost self-evident equations, since c, the number of moles per liter is the reciprocal of v_m, the number of liters per mole, in the equation $pv_m = \frac{p_0 v_0}{273} T = \frac{1 \times 22.4}{273} T = RT$, where $R = 0.08204$ liter-atmosphere;

$$p = 22.4 \times \frac{T}{273} c \text{ atmos}, \qquad p = cRT;$$

$$c = \frac{273 p}{22.4 T} \text{ moles per liter}, \qquad c = \frac{p}{RT};$$

i.e., the pressure of 1 mole per liter at 0° (since in 22.4 liters it is 1 atmosphere) is 22.4 atmospheres, and at $T°$ is $\frac{T}{273} 22.4$; while at 0° C., (273° absolute), the number of moles in one liter would be $\frac{1}{22.4}$ at 1 atmosphere pressure, or $\frac{273 p}{22.4 T}$ moles per liter at p atmospheres and $T°$ (i.e., $273 + t$).

In a mixture of two gases if the total pressure of the N $(= N_1 + N_2)$ moles is p, the partial pressure of the individual gases can be found from

$$p_1 : p :: N_1 : N$$
$$p_2 : p :: N_2 : N$$

(where p is the total pressure, and p_1 and p_2 are the partial pressures; while N is the total number of moles, and N_1 and N_2 are the constituent moles), for if the total number of moles N gives the pressure p, the number N_1 must give p_1.

We can thus define *the partial pressure of a gas, in a system of gases, as the ratio of the number of moles of that gas to the* *total number of moles in the system, multiplied by the total pressure.* In similar terms, of course, we can also define *the concentration of a constituent gas, in a system of gases, as the number of moles of that gas, divided by the total volume of the system.* These are the definitions we use in practical work, the above equations simply giving us the numerical relationship existing between them.

As it is quite necessary to become familiar with the use of these terms (and especially in their application to dissociation phenomena) for our later work, the following examples are given:

At 190° C. the reaction $PCl_5 \rightleftarrows PCl_3 + Cl_2$ goes to the right to such an extent that 44.3% of the original quantity of PCl_5 is decomposed, i.e., α, the degree of dissociation, is 0.443. Since we lose 0.443 of the pentachloride, and gain a like fraction of a mole of each of the trichloride and of chlorine, the final number of moles, starting with 1 of PCl_5, will be equal to

$$(1-0.443)+2\times 0.443, \text{ i.e., } 1.443.$$

The partial pressures may now be calculated, by dividing the number of moles of each constituent in the system, by the total number of moles present, and multiplying that ratio by the final pressure. We have, then, for the above case,

$$p_{PCl_5}=\frac{1-0.443}{1.443}\times p,$$

$$p_{PCl_3}=p_{Cl_2}=\frac{0.443}{1.443}\times p,$$

where p is the final pressure; 1 atmosphere, in case the volume increases to $1.443\times 22.4\frac{273+190}{273}$, and 1.443 atmospheres if it remains constant at the original, undissociated value, $22.4\frac{273+190}{273}$ liters, of the 1 mole.

To express the quantity of these three substances in terms of concentration (i.e., in moles per liter) it is only necessary to divide the final number of moles of each substance by the total volume of the system. Thus of the mole of PCl_5, with which we started, we have but $1-0.443$ mole left at equilibrium, and by the loss, gain 0.443 mole of each of the two constituents. Since, under the constant pressure of 1 atmosphere, the final volume of the entire system will be $1.443\times22.4\frac{273+190}{273}$ liters, the equilibrium concentrations will be

$$\frac{1-0.443}{1.443\times22.4\frac{273+190}{273}}=c_{PCl_5};$$

$$\frac{0.443}{1.443\times22.4\frac{273+190}{273}}=c_{PCl_3};\ =c_{\text{chlorine}}.$$

Here the volume has been assumed to change, retaining constant, atmospheric, pressure. In case the volume remains constant it is to be treated in the same way, for it is still the final volume. In the above case it would be $22.4\frac{273+190}{273}$ liters, i.e., the volume of the original mole at 1 atmosphere and 190°.

These constant pressure reactions can be assumed as taking place in a cylinder with a movable piston; the piston being held in its original position if the condition is to be constant volume.

Example.—10 grams of PCl_5 at atmospheric pressure are heated to 250° C., at which temperature α is equal to 0.8. Find the partial pressure and concentration of each of the three gases present at equilibrium, the pressure remaining constant.

If the PCl_5 were undissociated at this temperature the 10 grams would occupy $\frac{10}{208.7}22.4\frac{273+250}{273}$ liters, 208.7 being the molecular, molar, or formula weight of the PCl_5. Since $\alpha=0.8$, at equilibrium we must have $1.8\frac{10}{208.7}$ moles of the mixture of gases (i.e., $(1-\alpha+2\alpha)\ N$, where N is the original number of moles present, viz., $\frac{10}{208.7}\Big)$, in the final volume of

$$1.8\left(\frac{10}{208.7}22.4\frac{273+250}{273}\right) \text{ liters,}$$

the total pressure remaining constant at 1 atmosphere. The partial pressures, then, are $p_{PCl_5}=\frac{1-0.8}{1.8}$, $p_{PCl_3}=\frac{0.8}{1.8}$ and $p_{\text{chlorine}}=\frac{0.8}{1.8}$ atmospheres, since the term p, the total pressure, by which these terms should be multiplied, is 1 in this case. As there are $(1-0.8)\frac{10}{208.7}$ moles of PCl_5, $0.8\frac{10}{208.7}$ moles of PCl_3, and $0.8\frac{10}{208.7}$ moles of chlorine the final concentrations (moles per liter) are

$$\frac{(1-0.8)\frac{10}{208.7}}{1.8\left(\frac{10}{208.7}22.4\frac{273+250}{273}\right)}$$

for PCl_5, and

$$\frac{0.8\frac{10}{208.7}}{1.8\left(\frac{10}{208.7}22.4\frac{273+250}{273}\right)}$$

each for PCl_3 and chlorine.

Another, more complicated, illustration is the system

$$2NO_2 \rightleftarrows 2NO + O_2,$$

which, of course, can also be written

$$NO_2 \rightleftarrows NO + \tfrac{1}{2}O_2,$$

where in the first case 2 moles go to 3, while in the second 1 goes to $1\frac{1}{2}$. It makes no difference here which of these forms we use, for the concentrations and partial pressures will be found to be the same in both, the factor to transform one equation into the other cancelling in the ratios.

Thus, starting with 1 mole of NO_2 we would have, if α is the degree of dissociation, $2(1-\alpha)$ of NO_2, $2\times\alpha$ of NO and α of O_2 according to the first form; or $1-\alpha$ of NO_2, α of NO and $\frac{1}{2}\alpha$ of O_2 according to the second; i.e., the total moles by the first form is twice the number in the second. But the *total* number of moles in the system in the first is also twice as great as in the second, so that the concentration and partial pressure ratios would be the same according to both equations.

At 223° C., under constant atmospheric pressure, NO_2 is 5.3% dissociated according to the above equation. Starting with 1 mole of NO_2 at atmospheric pressure and 223° find the concentrations and partial pressures of NO_2, NO and O_2 at equilibrium.

Using the second form of chemical reaction given above, we have $1-0.053$ for NO_2, 0.053 for NO and $0.053\times\frac{1}{2}$ for O_2, all in moles. The total volume of the system, then, is the sum of these, multiplied by the volume of 1 mole under these conditions, i.e., $1.0265\times 22.4\times\frac{273+223}{273}$ liters = F.V. The concentrations, and partial pressures thus become,

$$c_{NO_2}=\frac{1-0.053}{\text{F.V.}}; \quad p_{NO_2}=\frac{1-0.053}{1.0265}\times$$

$$c_{NO}=\frac{0.053}{\text{F.V.}}; \quad p_{NO}=\frac{0.053}{1.0265}\times 1$$

$$c_{O_2}=\frac{0.0265}{\text{F.V.}}; \quad p_{O_2}=\frac{0.0265}{1.0265}\times 1.$$

Here if the volume had remained constant at what it is for 1 mole of undissociated NO_2 at that temperature and pressure, the following changes would be made in our calculation. The volume, instead of increasing under constant atmospheric pressure, would remain constant at $22.4\times\frac{273+223}{273}$ liters, and the concentrations would be equal to the moles of each constituent, divided by this the final (and also original) volume. Of course it is to be recognized here that α, under such conditions, could not be so large numerically as under 1 atmosphere pressure, for since the reaction normally goes forward with an increase in volume, the increased pressure brought about by retaining the volume constant would drive it backward in the opposite direction, and decrease α. The final pressure here, which, naturally, would be greater than the original, since the volume is held constant, is simply proportional to the number of moles present, for the greater the number of moles in a definite volume at constant temperature, the greater the pressure. If the total moles were 1.0265 (of course it would really be smaller), then the final pressure would be 1.0265 atmospheres, for 1 mole of undissociated NO_2 in this volume gave 1 atmosphere pressure. It would be necessary in getting the partial pressures of the constituents, then, to multiply the moles of constituent over the total moles, by this new pressure which is not 1, as it was above.

Of course, we can also consider chemical equations of the ordinary form in this way, as well as those giving involving a simple dissociation. In a chemical reaction of the type,

$$A+2B\rightleftarrows 3D+\tfrac{1}{2}E$$

(where the letters A, B, D and E represent the molecular weights of substances, in other words, are the weights of the various substance which are necessary to give equal gaseous volumes under like conditions) we must know not only the amounts of A and B we start with, but also the loss of either A or B which is necessary to carry the system into its state of equilibrium. Let us start, for example, with 1.5 moles of A and 1.70 moles of B, and assume that equilibrium is established when, at constant pressure (1 atmos.) and 103°, 0.6 mole of A is lost. We can find the concentrations and partial pressures then in the following way:

At equilibrium we must have $1.5-0.6$ of A, $1.7-(0.6\times 2)$ of B, $0+3\times 0.6$ of D, and $0+\frac{1}{2}\times 0.6$ of E; or 3.50 moles in total, produced from the original 3.2 (i.e., $1.5+1.7$) moles. Since the final volume at the constant pressure of 1 atmosphere is $\text{F.V.}=3.50\times 22.4\times\frac{273+103}{273}$ liters, we have

$$c_A=\frac{0.9}{\text{F.V.}};\quad c_B=\frac{0.5}{\text{F.V.}};\quad c_D=\frac{1.80}{\text{F.V.}};\quad c_E=\frac{0.30}{\text{F.V.}},$$

and

$$p_A=\frac{0.9}{3.50}\times 1;\quad p_B=\frac{0.5}{3.50}\times 1;\quad p_D=\frac{1.80}{3.50}\times 1;\quad p_E=\frac{0.30}{3.50}\times 1.$$

Here, just as in the previous example, constant volume would cause the pressure to increase and drive the reaction backward—and the concentrations and partial pressures could be calculated from the knowledge of the loss of A necessary to establish equilibrium, which, of course, would be smaller than the amount under constant pressure conditions; for of course the pressure under constant volume would be greater than it was originally. Thus if the volume were held constant at that occupied by the 3.2 original moles, and $1.5-x$, $1.7-2x$, $3x$, $\frac{1}{2}x$ were the new amounts in moles at equilibrium, where x is the loss of A (less than the 0.6 under constant pressure), the pressure would be p in the proportion

$$1 : p :: 3.2 : (1.5-x)+(1.7-2x)+3x+0.5x,$$

for the number of moles has increased above the 3.2 which in that volume gave 1 atmosphere pressure. We would have then,

$$p_A=\frac{1.5-x}{3.2+0.5x}\times p,\ \text{where}\ p=\frac{3.2+0.5x}{3.2}\ \text{atmos., etc.,}$$

and

$$c_A=\frac{1.5-x}{3.2\times 22.4\times\frac{273+103}{273}},\ \text{etc.,}$$

It must be borne in mind, here, in using the chemical reaction above, that it only refers to the *change* in the system, and has nothing to do with the absolute amounts necessary to react. Thus it simply provides that *if* A and B react, 1 mole of A *must* unite with 2 of B, to form 3 of D and $\frac{1}{2}$ of E—but it has nothing to do with the amounts of A and of B we start with. We can start, if we please, with any amounts desired of these, but can only use the equation when we know these amounts, and also the amount of one of them lost; then, the chemical reaction shows us just how much of B is lost with the known loss of A (twice as many moles), and how much D and E are formed (viz., three times as many moles of D, and $\frac{1}{2}$ as many of E, as are lost of A).

Specific heat. The first principle of thermodynamics.—When heat energy is applied to a body the temperature rises. The ratio of the amount of heat supplied to the consequent rise in temperature is called the *capacity of the body for heat.* The value of this term depends naturally upon the original temperature of the body, its pressure, etc.

The specific heat of any substance is the capacity for heat of the unit of mass, i.e., *is the amount of heat necessary to raise the temperature of 1 gram of it 1° C.*

It has been observed that the specific heat of a gas depends upon the conditions under which it is determined. If the gas is allowed to expand under its previous pressure, the specific heat, s_p, is different from that obtained when the pressure varies, and the volume remains constant, s_v. Before considering the reason for this, and finding the relation between the two values, it will be necessary for us to inquire into the nature of heat energy and its possible transformations.

Mayer in 1841 was the first to develop the subject of the theory of heat and its transformations, or Thermodynamics, as we know it to-day. Before that date heat was considered as an actual substance, *caloric*, which could be made to enter or leave a body. Mayer first recognized heat as an energy, which could be obtained from any other energy or transformed into the latter; his principal work was to determine the mechanical equivalent of heat, i.e., a factor by which an amount of heat energy can be expressed in units or terms of mechanical energy. He was led to this conclusion by the point already mentioned, that the specific heat of a gas under constant pressure is always larger than the specific heat of the same gas for constant volume. His reasoning was as follows: Since the specific heat at constant pressure is always greater than that for constant volume, there must be some condition in the former state which absorbs this extra heat. In the case of constant pressure the volume increases, and work must be done to overcome the atmospheric pressure, which would otherwise keep the volume constant. It is a logical consequence, then, to consider that this extra heat is simply the amount necessary to do the mechanical work of expansion. In other words, a certain number of calories are found to be equal to a definite number of mechanical units; this value for one calorie is the *mechanical equivalent of heat.* The numerical value of this term may be calculated as follows: The difference between the heats necessary to raise the temperature of 1 gram of air 1° C. under the two conditions is, by experiment,

$$s_p - s_v = 0.0692 \text{ cal.}$$

This 0.0692 cal. is the heat which is equivalent to the work necessary to expand 1 gram of air 1/273 of its volume at 0°, since a gas when heated 1° increases its volume under constant pressure by an amount equal to 1/273 of its volume at 0°, according to the law of Charles. Imagine 1 gram of air at 0° enclosed in a tube with a cross-section of 1 square centimeter. It will occupy the space of 773.3 cms., if the pressure is 76 cms., for this is the specific volume of air, i.e., the volume occupied by 1 gram under these conditions. An increase of temperature of 1° will expand this volume $773.3 \times 1/273$, i.e., 2.83 cms. The weight of the atmosphere, 1033.6 grams per square centimeter, will then be raised through this distance. The work necessary to do this is

$$1033.6 \times 2.83 = 2925.1 \text{ gr.-cms.},$$

which must be equivalent to the 0.0692 calorie. For one calorie, then, we have

$$\frac{2925.1}{0.0692} = 42,270 \text{ gr.-cms.},$$

which is called the *mechanical equivalent of heat.*

Joule transformed a known amount of mechanical work into heat by friction, and found from the heat developed that

$$1 \text{ cal.} = 42{,}355 \text{ gr.-cms.}^*$$

The great consequence of Mayer's work is the recognition of what is known as the first principle of thermodynamics, or the principle of the conservation of energy. According to this *the energy of any isolated system is constant*, i.e., when energy seems to disappear it is simply transformed into another form. If, for example, a gaseous body is heated, its internal energy is increased; if the volume increases, however, a certain amount of this heat is used to overcome the atmospheric pressure, and the increase of the internal energy is less than would otherwise be the case. If U is the internal energy and the amount of heat dQ is supplied to the body, then

$$(2) \qquad dQ = dU + dW,$$

where dW is the amount of work done by the body by virtue of the heat absorbed, and dU is the corresponding increase in the internal energy. If we consider the work as overcoming a resistance it is more readily handled. Suppose the gas to

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* Since a liter-atmosphere is the work necessary to force the weight of the atmosphere, upon a square decimeter, through a decimeter, we have

$$1 \text{ L. A.} = \frac{1033.6 \times 10 \times 100}{42600} = 24.26 \text{ cals.},$$

42,600 being value of the mechanical equivalent of heat now used, the average of a number of late determinations.

R, the molecular gas constant, which is equal to 84,780 gr.-cms., or 0.08204 L. A., is equal practically to 2 cals, i.e., to 1.9885 cals.

If the reader cannot follow the mathematics involved in the derivation of the following formulas, he can simply turn to their physical meaning, which is given below them in italics, and will thus be able to use the important relations, even though he cannot derive them.

increase its volume, the pressure remaining constant; then for 1 mole

$$dW = pdv_m,$$

where p is the intensity factor and v_m the capacity factor of volume energy. Substituting this value of dW in the former equation (2), we have

$$(3) \qquad dQ = dU + pdv_m,$$

where dU, dQ, and pdv_m are expressed in absolute units. If dU and pdv_m are given in mechanical units, then, (3) becomes

$$(4) \qquad dQ = \frac{dU + pdv_m}{J},$$

where J is the above mechanical equivalent of heat, i.e., the value in mechanical units of 1 calorie. We shall use the form (3), however, always remembering that dQ, dU, and pdv_m are to be expressed in the same units. The internal energy U of a gas may be considered as a function of pressure and volume, of pressure and temperature, or of volume and temperature. Of these we shall only consider the case where temperature and volume are variable. We have then

$$dU = \frac{dU}{dT}dT + \frac{dU}{dv_m}dv_m.$$

The term $\frac{dU}{dv_m}dv_m$, however, is equal to zero, for the internal energy of a gas, according to Gay-Lussac's experiment, remains the same after a change in volume provided no external work is done. By this experiment it was shown that the expansion of a gas into a vacuum does not change the temperature of the system; although there is a slight increase in the temperature of the exhausted vessel and a slight decrease in the other, they compensate one another. Equation (3) becomes then

$$dQ=\frac{dU}{dT}dT+pdv_m.$$

If v_m is constant, i.e., $dv_m=0$, then

$$dQ=\frac{dU}{dT}dT.$$

This term, $\frac{dU}{dT}$, the increase in the internal energy caused by an increase of temperature, is, however, the molecular specific heat for constant volume, i.e., $M\times s_v=S_v$; hence

$$dQ=\frac{dU}{dT}dT=S_v dT \text{ (for constant volume).}$$

If the pressure remains constant and the volume varies, i.e., if dv_m does not equal zero, then pdv_m does not disappear, and we have

$$dQ=S_v dT+pdv_m, \tag{5}$$

or

$$\frac{dQ}{dT}=S_v+\frac{pdv_m}{dT}.$$

This term, $\frac{dQ}{dT}$, under these conditions is the specific heat at constant pressure, for it includes the external work, i.e.,

$$S_p=\frac{dQ}{dT}=S_v+\frac{pdv_m}{dT}. \tag{6}$$

By differentiating (1), p remaining constant, we have

$$pdv_m = RdT,$$

or

$$R = p\frac{dv_m}{dT}.$$

Substituting this in (6), we find

$$S_p = S_v + R, \tag{7}$$

when S_p and S_v refer to the specific heats for 1 mole of gas, and R is the molecular gas constant.

If in the system no heat is absorbed or given up by conduction or radiation, i.e., $dQ = 0$, we have *an adiabatic process.* From (1), by complete differentiation, we have

$$pdv_m + v_m dp = RdT.$$

If in (5) we eliminate dT, by this equation, remembering that

$$S_v + R = S_p,$$

we obtain

$$dQ = \frac{S_v}{R}v_m dp + \frac{S_p}{R}pdv_m. \tag{8}$$

Since in an adiabatic process, $dQ = 0$,

$$0 = \frac{S_v}{R}v_m dp + \frac{S_p}{R}pdv_m. \tag{9}$$

And, representing the ratio of the specific heats, $\frac{S_p}{S_v}$, by γ (for air $= 1.41$), we have

$$v_m dp + \gamma pdv_m = 0,$$

or

$$\gamma\frac{dv_m}{v_m} + \frac{dp}{p} = 0.$$

And by integrating between the limits p, v_m, and p_1, $v_{m,1}$, we have

$$\log_e p + \gamma \log_e v_m = \log_e p_1 + \gamma \log_e v_{m,1},$$

i.e.,

$$\gamma = \frac{\log_e p_1 - \log_e p}{\log_e v_m - \log_e v_{m,1}}, \tag{10}$$

or, in another form,

$$\frac{p}{p_1} = \left(\frac{v_{m,1}}{v_m}\right)^{\gamma}.^{*} \tag{11}$$

From (11) we see that for an adiabatic process the volume changes less for a change in pressure, or the pressure changes more for a change in volume, than is the case when the temperature remains constant (i.e., an isothermal process). *For rapid compressions or expansions of a gas, then, we have the relation,*

$$p_1 : p :: v_m^{\gamma} : v_{m,1}^{\gamma},$$

where $\gamma = \frac{S_p}{S_v}$ *is the ratio of specific heat at constant pressure to that at constant volume; in place of*

$$p_1 : p :: v_m : v_{m,1},$$

which is true when the process is very slow, and the temperature consequently remains constant owing to radiation.

Boyle's law holds also of course for an adiabatic change, *after* the temperature produced by the change of volume has been reduced to the original one.

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* $\left(\frac{v_{m,1}}{v_m}\right) = \left(\frac{v_1}{v}\right).$

In equation (11) we know that

$$pv_m = RT$$

and

$$p_1 v_{m,1} = RT_1;$$

hence

$$\frac{pv_m}{p_1 v_{m,1}} = \frac{T}{T_1}.$$

But, by (11)

$$\frac{v_m}{v_{m,1}} = \left(\frac{p_1}{p}\right)^{\frac{1}{\gamma}}.$$

Whence, by substitution,

$$\frac{T}{T_1} = \left(\frac{p}{p_1}\right)^{\frac{\gamma-1}{\gamma}}. \tag{12}$$

By substituting $\left(\frac{v_{m,1}}{v_m}\right)^{\gamma}$ for $\frac{p}{p_1}$, here, we obtain

$$\frac{T}{T_1} = \left(\frac{v_{m,1}}{v_m}\right)^{\gamma}. \tag{13}$$

The temperatures to be obtained by the free expansion of a gas at the temperature T can be found from (12). Examples of this are given in the table below, where T is 273, and p_1 is 1 atmosphere, the values of T_1 and p being given.

TEMPERATURES CAUSED BY ADIABATIC EXPANSION OF AIR *

$\gamma = 1.4$

Intital Temperature = 0° C.

p (atmospheres).	t° Centigrade.	T° absolute.
100	−199.9	73.1
200	−213.0	60.0
300	−219.6	53.4
400	−223.8	49.2
500	−226.8	46.2

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* For other calculations involving the above formulas, see Falk, Jour. Am. Chem. Soc., 28, 1517, 1906, and 29, 1536, 1907.

The temperatures are those of the air as it expands. Owing to the high specific heat of the vessels used, it is impossible to reach these temperatures in anything in contact with the gas, although very low temperatures may be thus obtained.

The idea involved in equation (7) is a very valuable one; it can also be derived in the following simple way. The difference between the molecular heat at constant pressure and that at constant volume is obviously equal to the heat equivalent of the work of expansion, for the constant pressure condition involves external work, while the constant volume condition is a no-external-work condition. By definition, however, the external work done in the formation of a mole of any gas from negligible volume, against any constant pressure, at the temperature T, is RT. At the temperature $T+1$, the external work of formation of a mole would be would be $R\ (T+1)$; hence the work done by the expansion of 1 mole of any gas, on the heating of 1°, must be equal to

$$R(T+1)-RT=R,$$

hence

$$M(s_p-s_v)=R=2 \text{ cals.},$$

or

$$S_p-S_v=R=2 \text{ cals.}$$

The molecular specific heat (molecular weight times specific heat) at constant pressure, less that at constant volume, is a constant value for all gases, and equal to R or 2 calories.

Naturally the terms Ms_p and Ms_v (or s_p and s_v) here, are to be determined at the same temperature. That this relation holds experimentally is shown by the following list of determined values (Clausius-Ostwald).

MOLECULAR SPECIFIC HEATS

Name.	Const. Pres.	Const. Vol.	Ratio (γ).
Oxygen	6.96	4.96	1.40
Nitrogen	6.93	4.83	1.41
Hydrogen	6.82	4.82	1.41
Chlorine	8.58	6.58	1.30
Bromine	8.88	6.88	1.29
Nitric oxide (NO)	6.95	4.95	1.40
Carbon monoxide	6.86	4.86	1.41
Hydrochloric acid	6.68	4.68	1.43
Carbon dioxide	9.55	7.55	1.26
Nitrous oxide (N_2O)	9.94	7.95	1.25
Water	8.65	6.65	1.28
Sulphur dioxide	9.88	7.88	1.25
Ozone	—	—	1.29

VALUES OF $\gamma = \frac{s_p}{s_v}$ OF GASES

He	1.67	CH_4	1.32
Ar	1.67	C_2H_4	1.24
Hg	1.67	CS_2	1.20
Air	1.40	$CHCl_3$	1.15
HI	1.40	C_2H_5OH	1.13
NO_2	1.27	C_6H_6	1.11
H_2S	1.33	$(C_2H_5)_2O$	1.06

This relation gives us another (pp. 3, 10) definition of molecular or formula weight in the gaseous state. *The molecular or formula weight of a gas is that number which when multiplied by the difference between the specific heat at constant pressure and that at constant volume gives a value of 2 calories.*

The ratio $\gamma = \frac{s_p}{s_v}$ of equation (11) is also employed to find the number of combining weights contained in a formula weight of a gas. This is purely an empirical relation, it having been observed that known *monatomic gases, mercury for example,* *give* $\gamma = 1.667$, *diatomic ones about 1.4, triatomic about 1.29, etc.; the greater the number of atomic weights to the formula weight, the smaller the value of the relation* $\frac{s_p}{s_v}$, *approaching 1 as the lowest limit.* An example of this application is given by Ramsay in the work on argon, where the atomic or combining weight, owing to the non-existence of any compounds with this, is unknown. Here, however, finding the ratio $\gamma = \frac{s_p}{s_v} = 1.67$, and knowing from density determinations the molecular weight, he was able to show that the gas is monatomic, i.e., its atomic weight is equal to its molecular weight, viz., 40.

By combining the equation

$$M(s_p - s_v) = 2$$

with the value of the relation $\frac{s_p}{s_v}$, for the gas in question, it is apparent that, so long as the gas laws hold, the value of Ms_v (or of Ms_p) is the same for all so-called monatomic gases. Naturally Ms_p (or Ms_v) will have a different value for a diatomic gas, but that value will also remain constant, under the above condition, for all diatomic gases; and the same is true when for all triatomic, etc., gases. In this way it is possible to get an approximate value of s_p or s_v for any gas simply from the knowledge of the constant value, Ms_p (or Ms_v) for that type of gas, and the molecular weight of the gas.*

Determination of the specific heat of gases.—The specific heat of a gas at constant volume s_v cannot be determined directly with accuracy, since the vessel containing the gas

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* Delaroche and Berard first found this for diatomic gases in the form

$$M's_p' = M''s_p'' = M'''s_p'''$$

or

$$M's_v' = M''s_v'' = M'''s_v'''.$$

absorbs so much more heat than the gas itself. Even under the most favorable conditions here the ratio of the absorption of heat by the gas to that by the vessel is as 1 is to 55.

From the specific heat at constant pressure and the value of the ratio $\gamma=\frac{s_p}{s_v}$, s_v can, however, be found indirectly; or, knowing the molecular weight of the gas and its specific heat at constant pressure, from experiment, we can calculate s_v from $M(s_p-s_v)=2$.

The specific heat at constant pressure is determined by passing a certain volume of the gas, heated to a certain temperature, through the worm of a calorimeter under a constant pressure, and observing the consequent increase in the temperature of the water. We know then the number of calories which causes a certain temperature to exist in the known weight of the gas; and from these data it is easy to calculate the specific heat, s_p. For monatomic gases it has been observed that the value of the molecular specific heat at constant pressure, $Ms_p=S_p$, is not only independent of the temperature, but is the same for all gases of that type; and the same therefore must be true of the molecular specific heat at constant volume, s_v. Here we find $Ms_p=5$ and $Ms_v=3$ calories. The value of the molecular specific heat at constant pressure for a number of gases, other than the monatomic ones, seems to converge toward the value 6.5 at the absolute zero. We have in general, then, the relation [*]

$$Ms_p=6.5+aT,$$

where a is a constant for each gas and is the larger, the more complex the formula. For a we find the following values: for H_2, N_2, O_2, and CO, HCl, HBr, HI and NO, $a=0.001$, $C_6H_6=0.0510$, ether$=0.0738$, $C_2H_4=0.0137$, $CHCl_3=0.0305$,

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[*] For a résumé of the variation of S_p (i.e., Ms_p) with the temperature for a number of gases, see Lewis and Randall, Jour. Am. Chem. Soc. 34, 1128, 1912.

$C_2H_5Br = 0.0324$, $CH_3COOC_2H_5 = 0.0674$, $C_3H_6O = 0.0403$, $N_2O = 0.0089$. This formula may be used in the following way to find the value s_p. For C_6H_6, $a = 0.0510$; hence at 50°, we have

$$s_p = \frac{6.5 + 0.0510 \times 323}{78} = 0.295,$$

while Wiedemann found 0.299 experimentally.

The effect of increased pressure upon the value of the specific heat at constant pressure of a gas is apparently to increase it. In the following table are grouped a few values of s_p determined under various pressures, at the same temperature.

EFFECT OF PRESSURE UPON s_p

Air.		H_2.		CO_2.		N_2O.		C_2H_4.		CH_4.	
p.	s_p.	p.	s_p.	p.	s_p.	p.	s_p.	p.	s_p.	p.	s_p.
40 at.	0.274	1 at.	3.402	1 at.	0.201	1 at.	0.225	1 at.	0.404	1 at.	0.591
70 at.	0.312	30 at.	3.788	30 at.	0.267	30 at.	0.278	30 at.	0.450	30 at.	0.692

The value of the ratio $\gamma = \frac{s_p}{s_v}$ can be found easily by the method of Clément and Desormes, even though the individual values of s_p and s_v are unknown.

A glass balloon, holding about 20 liters, is provided with a brass stop-cock and a manometer. From this vessel the air is partially rarefied and the pressure observed by aid of the manometer. Let this initial pressure be p_0 and the atmospheric pressure be p. If the cock is now opened and closed again rapidly, air will rush in until the external and internal pressures are the same. As the air goes in, however, heat will be developed, which, as it is not removed, will increase the temperature of the gas according to the law of adiabatic compression (p. 53). By the process we have increased the pressure from p_o to p. If the initial specific volume is $v_{s,o}$ and the final one is v_s, then γ can be determined from the equation

$$\frac{p}{p_o}=\left(\frac{v_{s,o}}{v_s}\right)^{\gamma}.$$

The final specific volume, v_s, is not known yet, however. To find this we wait until the flask and air have been reduced to the temperature of the surrounding air and again measure the pressure. If this pressure is p' at the temperature t, then

$$v_{s,o} : v_s :: p' : p_o,$$

or substituting the $\frac{p'}{p_o}$ for the $\frac{v_{s,o}}{v_s}$ above,

$$\frac{p}{p_o}=\left(\frac{p'}{p_o}\right)^{\gamma};$$

and we finally obtain

$$\gamma=\frac{\log p-\log p_o}{\log p'-\log p_o}.$$

In one experiment with air $p=1.0036$, $p_o=0.9953$, and $p'=1.0088$ atmospheres; hence

$$\gamma=1.3524.$$

Another method for the determination of γ $\left(=\frac{S_p}{S_v}\right)$ is that employing the Kundt tube, and measuring the length of sound waves in various media as they are reproduced by a layer of cork filings in the bottom of the tube. A description of this well-known method will be found in any text-book of Physics.

The question now arises as to the change in $\gamma=\frac{S_p}{S_v}$ with pressure and temperature. Here again we exclude the monatomic gases, for which it is constant. Experiment shows here that for other gases the value increases considerably with increased pressure. A few of the observed values under various conditions are given in the table below.

EFFECT OF PRESSURE UPON $\gamma=\frac{s_p}{s_v}$ AT CONSTANT TEMPERATURE

AIR $t=-79°$ C.		CO₂.		
p.	γ.	p.	t.	γ.
1 atmos.	1.405	$\frac{1}{3}$ atmos.	15°	1.279
25 “	1.569	1 “	20°	1.300
50 “	1.767	50 “	50°	1.705
100 “	2.200	60 “	50°	1.903
150 “	2.469	70 “	50°	2.327
200 “	2.333			

γ for air is found to be constant under 1 atmosphere pressure from 0° to 900° within 1%; for CO_2 the variation between these limits is found to be 3.5% while for SO_2 it is 4.8%. For the monatomic gases Na and K Robetzsch (Ann. Phys. (IV), 38, 1027) finds respectively the values 1.68 ± 0.03 between 750°–920°, and 1.64 ± 0.007 between 680°–1000°. (For a list of some values of γ see the table on page 56.)

It is evident, of course, that our relationship $M(s_p-s_v)=2$, must depend for its holding on the holding of the gas laws; in other words, it is only to be depended upon when $pv_m=RT$, whether or not the values of the specific heats, s_p and s_v, themselves change in the same way with changes in pressure and temperature. For we have seen enough in the illustrations under the Van der Waals' equation, of the variation of the observed product pv with the conditions, to conclude that uncorrected, as provided for there, the product could not continue to be constant and equal for all gases.

The second principle of thermodynamics.—By the first principle we have found that a certain amount of heat is always equivalent to a certain amount of work. If we consider, however, the possible means of transforming heat into work we find that a certain condition must be fulfilled, i.e., that the heat will always go of itself from a warmer to a colder body. In other words, heat can only produce work by going from a higher to a lower temperature, and work must be done upon a system to cause heat to go from a colder to a warmer body. This condition is usually expressed as follows: *Heat of itself can never go from a colder to a warmer body without work being done to cause it; a perpetual motion of the second kind is impossible.*

A device to produce a perpetual motion of the second kind would be a machine which would run, for example, from the heat of the sea, and allow the heat of this, at its low temperature, to be abstracted and employed in a system at a higher temperature. It is related to the second principle just as an ordinary perpetual motion is related to the first principle.

Since heat can only be transformed into work by a transference of heat from a higher to a lower temperature, it is important to know the relationship which exists between the amount of heat transferred as heat and that transformed into work. Heat can only be transformed into mechanical work through the agency of a gas. Thus if a gas at room temperature and under a high pressure is allowed to do work by expanding under a reduction of pressure, the gas will cool, heat equivalent to the work being removed and thus lowering the temperature of the gas. When the temperature is lower than that of the atmosphere, however, there will be a transfer of heat from the warmer air to the cooler gas, until the temperature of that is once more equal to the original, i.e., the air, temperature. We can say, then, that the fall of the amount of heat involved, through the number of degrees measuring the difference in temperature observed, has done the required amount of work.

A definite number of calories falling through a certain number of degrees then, is observed to do work. And we have only to find an expression correlating the work done, and the number of degrees of fall necessary to do it, under various conditions.

For this investigation it is necessary that all the work done be external work, which can be readily observed, and then compared with the known amount of heat. We employ for this purpose a process originated in 1824 by Carnot, which is known as the Carnot cycle. The arrangement is such that the final state is identical with the initial one, i.e., before and after the operation the body contains exactly the same amount of energy. Then the relation between the heat transferred and the work done is very readily obtained. Naturally no heat must be lost by radiation or conduction, or the final result will be incorrect; for this reason the process is an ideal one and cannot be realized practically. Since all transference of heat and work is assumed to take place without differences in temperature and pressure, the process may go in either direction, i.e., it is reversible. This condition of reversibility is never perfectly obtained in practice, however, so that the relation which we find is the limit under the most favorable conditions.

The thermodynamic Cycle.*—A gas, on absorbing heat, expands and does work until its temperature, which must have been higher than that of the environment, falls to this. By this process heat at a high temperature is absorbed by the gas and partly transformed into external work. When the temperature of the gas is reduced to that of the environment no more work can be done unless the pressure of the system is still greater than that of the surroundings. The object of this process we are to assume as carried out is to find the relation of heat absorbed to the heat which is transformed into work under ideal conditions.

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* If the reader does not follow the mathematical derivation, he may simply turn to the physical meaning of the relation derived so that he can at least make use of it.

1. Assume 1 gram of an ideal gas enclosed in a cylinder with a movable piston at a certain temperature and pressure. The cylinder is first placed in a heating-bath at the temperature T_1, and the volume is allowed to increase under a constant pressure, which is just greater than that of the atmosphere. By this expansion the gas will cool. Here, however, we assume heat to be absorbed by it to such an extent that the temperature remains constant. If the heat absorbed by the gas is Q_1, its initial specific volume v_s', and its final one v_s'', and the constant temperature is T_1, then the work done by the gas will be equal to $\int_{v_s'}^{v_s''} pdv_s$. Since the temperature remains constant, equation (5) becomes

$$dQ_1 = 0 + pdv;$$

or, since $p = \frac{rT}{v_s}$,

$$dQ_1 = rT\frac{dv}{v_s}$$

or

$$Q_1 = rT_1 \log_e \frac{v_s''}{v_s'}. \tag{14}$$

2. The gas is then allowed to expand adiabatically until the temperature falls to T_2. For this, the new volume being v_s''', we have the relation

$$\frac{T_1}{T_2} = \left(\frac{v_s'''}{v_s''}\right)^\gamma. \tag{15}$$

3. Next the pressure is increased until the volume decreases to v_s^{IV}, heat being removed to the amount Q_2, so that the tem-

perature remains constant at T_2. The work done here by the gas is $-\int_{v_s'''}^{v_s^{\text{IV}}} pdv$; we have then

$$(16) \qquad Q_2 = rT_2 \log_e \frac{v_s'''}{v_s^{\text{IV}}}.$$

4. Finally, the gas is compressed adiabatically until the original volume v_s' and the original temperature T_1 are reached. This can be arranged by choosing v_s^{IV} of the proper size. We have for this relation

$$(17) \qquad \frac{T_2}{T_1} = \left(\frac{v_s'}{v_s^{\text{IV}}}\right)^{\gamma}.$$

We have thus carried the gas through a series of changes, and have finally the same state as that from which we started. The amount of heat Q_1 is absorbed at the higher temperature T_1, and a smaller amount Q_2 is given up at the lower temperature T_2, and a certain amount has been transformed into work. The amount of heat which is equivalent to the work done is, therefore, equal to $Q = Q_1 - Q_2$; while the heat Q_2 has simply been transferred from the temperature T_1 to T_2.

The relation between Q_1 and Q_2 is given by equations (14) and (16)

$$\frac{Q_1}{Q_2} = \frac{rT_1 \log_e \dfrac{v_s''}{v_s'}}{rT_2 \log_e \dfrac{v_s'''}{v_s^{\text{IV}}}}.$$

By (15) and (17), however,

$$\frac{v_s''}{v_s'} = \frac{v_s'''}{v_s^{\text{IV}}}, \quad \text{i.e.,} \quad \log_e \frac{v_s''}{v_s'} = \log_e \frac{v_s'''}{v_s^{\text{IV}}};$$

hence

$$\frac{Q_1}{Q_2} = \frac{T_1}{T_2},$$

i.e., *the amounts of heat absorbed and liberated during the process are proportional to the absolute temperatures.*

The amount of heat transformed into work is $Q=Q_1-Q_2$. We have then

$$\frac{Q_1-Q_2}{Q_2}=\frac{T_1-T_2}{T_2}$$

and .

$$\frac{Q_1-Q_2}{Q_1}=\frac{T_1-T_2}{T_1}.$$

From the two equations above we may conclude that, in reversible processes, *the work done, or to be done, by the transformation of heat into work is to the amount of heat absorbed at the temperature T_1 (or liberated at T_2), as the temperature interval through which the heat has fallen (or must fall), is to the absolute temperature T_1 (or T_2).*

Thus at a boiler temperature of 200° and a condenser temperature of 50°, the fraction of the heat absorbed which would be transformed into work under ideal conditions is $\frac{150}{273+200}$, and the ratio of heat transformed into work to the heat evolved as heat at T_2 is, at greatest, $\frac{150}{273+50}$. *If T_2 were the absolute zero, then, and only then, all heat absorbed would be transformed into work;* otherwise the ratio is always less than 1. Naturally, in the above, both heat and work must be expressed in the same units.

Although we have derived this relation for gases it is equally true for all systems where heat is being transformed into any kind of work.

It will be seen from the above that the first principle of thermodynamics shows us just how heat will be transformed into work, *when it is transformed;* while the second law shows us the conditions *necessary in order that heat may be transformed into work.*

The kinetic theory of gases.*—The fundamental idea of the kinetic theory of gases, which was developed by Krönig (1856) and Clausius (1857), is that it is possible to derive the laws for gases on the assumption that the structure of a gas is not continuous, but that it is made up of discrete particles or molecules, which themselves are composed of smaller particles, the atoms. If a gas is composed of molecules, which are in continuous and rapid motion in straight lines, then gaseous pressure can be regarded as being produced by the bombardment of these particles upon the walls of the vessel.

Assuming the mass of the gas-particle (molecule) to be designated by m, and its velocity by u, each collision with the wall of the vessel will exert a force mu; and since the molecule, if it be assumed to be perfectly elastic, will receive back all the energy involved, its momentum, as it rebounds, will be the same as before, but of the opposite sign. The amount of force exerted on two opposite parallel walls, then, will be $2mu$. Let us consider the gas to be enclosed in a cubical vessel, with an edge of the length l, and assume the number of molecules present to be n, and that their motion takes place in every direction. Since any velocity may be resolved into its three components, parallel to the edges of the cube, the diagonal of which represents the velocity, we have for the average velocity of the particle,

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* This section, with additions, has been taken from the second edition of this text (it having been eliminated in the third and fourth editions) in order that the reader, having finished for the present the discussion of the gaseous state, may now gain a general idea of the more hypothetical form of theoretical reasoning, in addition to the empirical and thermodynamical forms used up to now. It must be remembered here, however, that because the results of the reasoning agree with experiment, it is no certain proof that the premises are the correct and only ones, for false premises often lead to correct results; as is shown by the number of correct deductions made in the theory of heat from the false premise that heat is an actual substance, caloric.

$$u^2 = u_1^2 + v_1^2 + w_1^2,$$

where the velocity components u_1, v_1 and w_1 may assume any value from o to u according to the direction. This expression means simply that the collision with a wall in one direction is equivalent to the combined effects of successive collisions on the walls in the three directions parallel to the components. Each molecule moving in the direction u_1, then, will produce a pressure on one wall equal to

$$mu_1\frac{u_1}{l},$$

where $\frac{u_1}{l}$ is equal to the number of wall collisions in the unit of time, for this is proportional directly to the velocity and inversely to the distance, which is l, the length of the cube-edge.

Since the action upon two parallel cube faces is

$$2\frac{mu_1^2}{l},$$

the total action upon all cube faces for any one molecule is

$$\frac{2m}{l}(u_1^2 + v_1^2 + w_1^2) = \frac{2mu^2}{l}$$

There are n molecules present, however, hence the total action upon the whole cube is

$$\frac{2mnu^2}{l}.$$

In measuring pressure, however, we would always refer to the unit of surface on one face of the cube, so in order to give the pressure, this expression must first be divided by $6l^2$. In this way we find

$$p=\frac{2mnu^2}{6l^3}=\frac{mnu^2}{3l^3},$$

but l^3 is plainly the volume of the cubical vessel, i.e., is the volume occupied by the gas. Assuming this volume to be that containing the molecular weight in grams, whereby n becomes the number of molecules in the gram-molecule or mole, we have then,

$$p=\frac{2mnu^2}{6v_m}=\frac{mnu^2}{3v_m}.$$

But for any one gas, certainly m, n and u at a constant temperature must be constant, hence

$$pv_m=\text{constant}$$

for any one gas—which is Boyle's law, that we have considered above.

If two gases are at the same temperature, under the same pressure, their kinetic energy, by definition, must be the same, i.e.,

$$\frac{mu^2}{2}=\frac{m'u'^2}{2};$$

and further if their volumes are the same, then $pv_m=pv_m'$; and since

$$pv_m=1/3mnu^2=2/3\frac{mnu^2}{2},$$

$$2/3\frac{mnu^2}{2}=2/3\frac{m'n'u'^2}{2},$$

which when combined with the previous equation, gives

$$n = n'.$$

i.e., *equal volumes of all gases under the same pressure and at the same temperature contain the same number of molecules.* This is the law we have referred to above as Avogadro's law when applied to the number of moles, and might be called, in this form, Avogadro's hypothesis. The number of molecules, n, is known as *Avogadro's number.*

Naturally, these equations, derived from the consideration of a cubical vessel, would also hold for vessels of other shape, for all other vessels can be regarded as being made up of a number of cubes—but the truth of them will depend, granting the existence of particles, in the perfect elasticity of the particle, for otherwise they would lose energy by each collision.

Solving the equation $pv_m = 1/3mnu^2$ for u the velocity of the molecule and consequently the speed of diffusion of the gas itself, when free to expand, we find

$$u = \sqrt{\frac{3pv_m}{mn}},$$

for which, since v_m/mn is equal to the reciprocal of the density of the gas, i.e., is the total volume, divided by the mass of the gas, we have

$$u = \sqrt{\frac{3p}{d}}.$$

The mean velocities of the molecules, i.e., *the speeds of diffusion, for example, of two gases, under like conditions, are inversely proportional to the square roots of their densities.* This law was discovered experimentally by Graham in 1833, and has been mentioned and used above on two occasions. In this way also it is possible to calculate what average speed the molecules of specific gases must have, with their assumed masses, to give the pressures we observe experimentally.

The term a in the equation of Van der Waals, in the light of the above is seen to be the specific attraction existing between the molecules of the gas; while b represents the volume occupied by the so-called working sphere of the molecules, themselves, i.e., of a volume estimated at four times that of the space occupied by the particles when so close together as to touch. As will be remembered in the practical use of that equation, b is the experimental volume-correction to be made to the volume of that weight of all gases which occupies 1 liter at 1 atmosphere pressure and 0° C., i.e., for $\frac{1}{22.4}$ of the molecular weight in grams of the gas.

Finally, applying these concepts of the kinetic theory to the consideration of the specific heat of gases, we find that since $pv_m = 1/3mnu^2 = 2/3\frac{mnu^2}{2}$ (where n is the Avogadro number, i.e., the number of molecules in 1 mole), and also $pv_m = RT$, the kinetic energy $\left(\text{viz., } \frac{mnu^2}{2}\right)$ of the molecular amount is equal to $3/2pv_m = 3/2RT = 3T$ calories.

If the gas is monatomic, at constant volume there can be no change produced in it by increased temperature outside the increased kinetic energy of the molecules; therefore when heated one degree, the amount of heat absorbed, i.e., *the specific heat of any monatomic gas at constant volume, for the molecular weight in grams, is*

$$3(T+1) - 3T = 3 \text{ calories} = S_v \text{ (for monatomic gases).}$$

When external work is done, in addition to the increase in kinetic energy of the molecules, we would have the specific heat at constant pressure. We know from page 57 that the specific heat S_p is always greater than that of S_v by 2 cals. (i.e., $M(s_p - s_v) = 2$ cals.), therefore the molecular specific heat at constant pressure for all monatomic gases is

$$3+2=5 \text{ cals.} = S_p \text{ (for monatomic gases).}$$

Combining these two values we find

$$\gamma = \frac{5}{3} = 1.667 \text{ (for monatomic gases),}$$

which is the value of γ we found above by experiment.

For polyatomic gases, it is assumed that heat is also absorbed by the atomic motions within the molecule. If this be true there must be an extra amount of heat absorbed in such cases, the amount depending upon the number of atoms in the molecule, and this is the same for any one gas, whether the volume is held constant, or is allowed to change. Calling this x for diatomic gases, and y for triatomic ones, for example, we would have

$$\gamma \text{ diatomic} = \frac{S_p + x}{S_v + x}; \quad \gamma \text{ triatomic} = \frac{S_p + y}{S_v + y},$$

where x must be smaller than y. If the above be true, the numerical value of γ diatomic should be less than 1.667, and larger than γ triatomic; for adding a constant to both numerator and denominator of a fraction greater than 1, causes the fraction to decrease in value the more, the larger the added quantity. All this is true experimentally, as will be seen by reference to the tables on page 56.

CHAPTER III.

THE LIQUID STATE.*

Distinction between liquids and gases.—Liquids are distinguished from gases by the fact that they possess a volume of their own, which, although dependent upon pressure and temperature, cannot be changed to any very considerable extent by them.

From the standpoint of experiment all we can say of the liquid state, as compared to that of a gas, is that it contains less energy than the latter, for energy is always absorbed by a liquid when it is being transformed into a gas at the same temperature. From the standpoint of the kinetic theory of gases, the attraction between the molecules of a liquid is said to be greater than that between those of a gas.

Since the volume in the gaseous state is always greater than that in the liquid state, a greater temperature is necessary to cause a liquid to boil when the pressure over it is increased. And, conversely, a liquid boils more readily (i.e., at a lower temperature), when the pressure over it is decreased. (See Le Chatelier's theorem, p. 33).

Connection between the gasesous and liquid states.—If at constant temperature a gas be subjected to a constantly increasing pressure, its state may change in one of two ways according to the conditions:

1. This case has already been considered under gases. The volume at first changes more rapidly than the pressure, next in the same ratio, and finally more slowly. When the

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*For numerical problems involving the principles disscused here, see Chapter X.

pressure becomes very high a further increase has but a slight effect upon the volume.

2. Here the relation between pressure and volume is quite different, although the first step is the same, i.e., the volume changes more rapidly than the pressure. The ratio here, however, in contrast to (1), increases continually. When a certain pressure is reached a new phenomenon is observed: the gas is no longer homogeneous; one part has separated which behaves differently from the rest, i.e., the gas is partly liquefied and we have both the liquid and gaseous phases present together. For a constant temperature this liquefying pressure remains constant, while the volume decreases steadily, i.e., for one pressure we have a whole series of volumes, dependent upon the relative amounts of gas and liquid present; for the volumes in the two states are different. An increase in the external pressure has no lasting effect upon the internal pressure of the system (which still remains as it was), but it causes the volume to decrease more rapidly, i.e., it increases the rate at which the liquid, of smaller relative volume, is produced from the gas. Only after the whole gas has been liquefied, and the liquid phase alone is present, can the pressure be increased. Then, however, we shall compress only the liquid, just as in the last stage of (1) we compressed the gas.

Whether a liquefiable gas shall behave as in (1) or in (2), is purely a question of the temperature. If the temperature is above a certain point, which can be definitely fixed for each gas, the gas will always behave as in (1), and the higher the temperature above this point, the more nearly will the gas follow the simple laws—in short, the more it will behave like the gases already considered in the illustrations given in the last chapter.

Below this temperature, however, the gas will always behave as in (2); and the lower the temperature below the characteristic point for the gas in question, the lower will be the pressure necessary to cause the liquid phase to appear. And the lower the constant temperature, the greater will be the volume change taking place as the gas is condensed to a liquid by the attempted increase in the internal pressure. The internal pressure, while the gas is condensing to a liquid, i.e., as long as the two states are present, always remains constant, however; excess of external pressure simply hastening the condensation. The more nearly we approach the characteristic temperature of the gas the smaller will be the volume change caused by the condensation at constant pressure, until finally just at this point, we find that the substance changes instantaneously and isothermally, and also *without change in volume* from the gaseous to the liquid state—and for each pressure, just as in (1), we have one definite volume only, viz., that of the gas up to a certain point, and that of the liquid above it; for the change has been continuous. Experimentally, here, it is observed that at one pressure we have homogeneous gas, while just above it we have homogeneous liquid, the latter being recognized by the instantaneous appearance of a meniscus, which on lowering the pressure again disappears instantaneously.

The phenomena described above were first recognized by Andrews in 1871. If, for example, we compress CO_2 gas, keeping the temperature at 0°, the volume changes more rapidly than the pressure, and at a pressure of 35.4 atmospheres the gas condenses with a change in volume, and at a rate, depending upon the magnitude of the external pressure we apply, to a liquid. The higher the temperature, under 30°.92, the higher the pressure must be to cause condensation; but above 30°.92 no condensation is possible. Thus:

t	*p*	*t*	*p*
31°,	impossible to liquefy it.	−21°	= 21.5 atmospheres.
30°.92	= 73.6 atmospheres.	−40°	= 11.0 "
30°	= 73.0 "	−59°.4	= 4.6 "
13°.1	= 48.9 "	−70°.6	− 2.3 "
0°	= 35.4 "	−78°	= 1.2 "

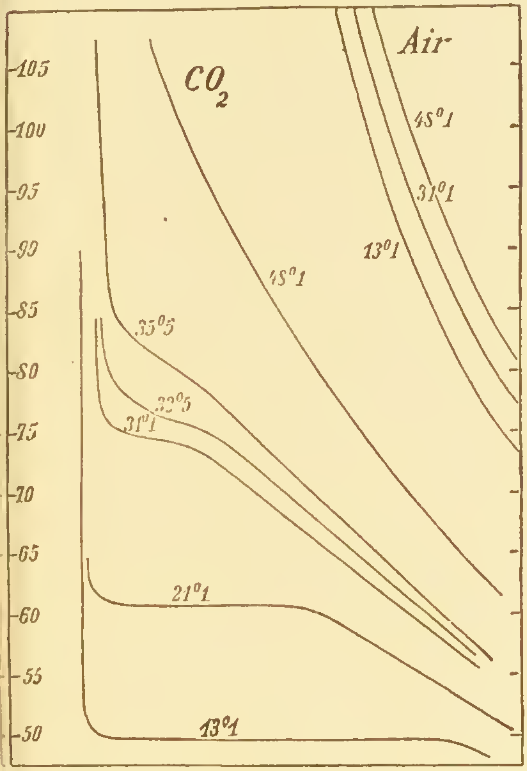
Andrews called the temperature 30°.92 the *critical temperature.* Correspondingly we call the pressure which is necessary to liquefy the gas, at the critical temperature, the *critical pressure* (73.6 atmos. at 30°.9 for CO_2), and the volume which the gas or liquid occupies ($v_l = v_g$), under these two conditions, the *critical volume.* Since all distinction between the two states disappears at the critical point, there is no energy difference between the two states, i.e., the heat of evaporation, from liquid to gas, at the same temperature, is zero; and consequently in general the numerical value of the heat of evaporation of the liquid must decrease with increased temperature, down to this zero value at the critical temperature.

The above table explains, of course, why CO_2 liquifies and then solidifies at atmospheric pressure when contained in a test-tube which is placed in liquid air—and in fact shows that even under a very much smaller pressure, at this very low temperature, it would also liquefy.

The best method of showing the behavior of a gas under compression is by plotting a curve in a system of coordinates where the pressures are laid out upon the axis of ordinates, and the volumes upon the axis of abscissæ. In such curves the horizontal parts would then show constant pressure for varying volume, and would indicate that the gas is liquefying, and that both liquid and gaseous phases are present. The vertical parts refer to the liquid state, while all others, except the horizontal, refer to the gaseous state.

The figure on p. 77 shows the behavior of CO_2 and air, the ordinates being pressures in atmospheres. At 31°.1 for CO_2 there is no horizontal part, i.e., no varying volume for constant pressure; the gas does not liquefy, since it is above its critical temperature. For all temperatures below 31°.1 the horizontal part is present, i.e., the gas liquefies under a sufficient pressure, and the lower the temperature the longer is the line showing the variation in volume at constant pressure, i.e., the greater is the difference in volume of the liquid and gaseous phases. Under all these pressures air remains a gas and behaves more as CO_2 does when above 31° C.

The behavior of CO_2 (or any other liquefiable gas) as given by the above description and experimental curves, is also indicated by Van der Waals' equation



$$\left(p+\frac{a}{v^2}\right)(v-b)=\frac{\text{constant}}{273}T,$$

which we found to apply so well to gases above their critical temperatures in the last chapter (pages 17–21), and in which v is the present volume of that weight of gas which occupied 1 liter at 0° C. (273° absolute) and 1 atmosphere pressure, p is in atmospheres, and a and b are constants for each gas, which can be found by experiment. Rewriting this equation in the form

$$p=\left(\frac{\text{constant}}{273(v-b)}\cdot T\right)-\frac{a}{v^2},$$

(where for CO_2, the values $b=0.0023$ and $a=0.00874$ are found to give exceedingly satisfactory agreements for the gas above its critical temperature at all pressures, and "constant" is equal to $p_o v_o$, i.e., to $(1+0.00874)(1-0.0023)=1.00643$, from the values at 273° (abs.) where p_o is 1 atmosphere and v_o is 1 liter) we find for all temperatures below 32°.5 C. that more than one assumed value of v leads to the same value of p, and that it is only at or above this temperature that every assumed value of v leads to its own distinctive value of the term p.

The table below presents the values of p as calculated from the above equation for certain assumed values of v, and shows that only at a temperature above 31° at any rate that the volume always corresponds to its own characteristic pressure; for in the other cases (i.e., below 35° C.) we find the same pressure for very different volumes.

CO_2.

$$p=\left(\frac{1.00643}{v-0.0023}\cdot\frac{T}{273}\right)-\frac{0.00874}{v^2}.$$

Volume was 1 at 273° (abs.) and 1 atmos.

v.	20° C. p (atmos.).	30° C. p.	31° C. p.	35° C. p.
0.1	10.2	10.6	10.6	10.7
0.05	19.1	19.9	20.0	20.3
0.015	46.2	49.0	49.3	50.5
0.010	52.8	57.6	58.0	59.9
0.009	53.2	58.6	59.2	61.4
0.0085	53.1	59.0	59.6	62.0
0.0080	52.7	59.2	59.8	62.5
0.0072	51.6	59.2	60.0	63.0
0.0065	50.2	59.0	59.9	63.4
0.0050	50.2	63.7	68.3	70.8
0.0040	88.9	110.4	112.7	121.4
0.0030	570.8	623.0	629.0	650.0

By the definite solution of the cubic equation, with respect to v, which was employed in the table, we find that 3 mathematical roots are possible, one of them plainly referring to the volume as liquid, another to the volume as gas, while the third has possibly no physical significance. Since at the critical temperature, we find experimentally that the volume as liquid is equal to that as a gas, let us solve the equation for v, on the assumption that the three possible mathematical roots (volumes) are identical, and see what relationship we shall find existing between the three critical quantities and the constants a and b at this point, i.e., where either the gas or liquid can exist alone, but not together, and where the volume of the former is equal to that of the latter. This point, it must be remembered, must then be the critical temperature, for below that the volumes of the liquid and gaseous states will always differ, and above it gas, alone, can exist. Designating the critical values of p, v, and T by the letters provided with the subletter c, we find, by solution of the cubic equation on the assumption that the three roots are identical that

$$v_c=3b;\quad p_c=\frac{a}{27b^2};\quad \text{and}\quad T_c=\frac{8a}{27b\,\dfrac{\text{constant}}{273}},$$

where $\dfrac{\text{constant}}{273}=\dfrac{1.00643}{273}=0.003687$ for CO_2. (In general it may be considered as practically 0.00366, i.e., $\dfrac{1}{273}$.)

In other words, then, *from the constants a and b of Van der Waals' equation, which can be determined from the behavior of the gas under compression at any temperature, it is possible for us to calculate the critical temperature, pressure and volume of the gas.* Solving the above equations for CO_2 we find $T_c=305^\circ.4$ abs. (i.e., $32^\circ.5$ C.), $v_c=0.0069$, and $p_c=61.2$ atmospheres, while experimentally we find $t_c=30^\circ.9$; $v_c=0.0066$ and $p_c=70$. v_c here, it is to be remembered, represents only the *relative volume* at the critical state of both gas and liquid, of that weight of gas which occupied 1 liter at 0° C. and 1 atmosphere (i.e., of $\frac{1}{22.4}$ of the molecular weight). The *critical density*, on the other hand, d_c is a quantity expressed in terms of water at 4°; in other words actually represents the weight in grams of 1 cc. of either liquid or gas.

Although the agreement is not always especially good when we apply Van der Waals' equation in this way, it is indeed striking that a law derived to represent the variation from the simple gas laws should lead to a relationship enabling us to calculate the values of the critical constants, even if in some cases the results are burdened with an error.

Since these critical values are dependent upon the Van der Waals constants a and b of the gas, it is of course possible for us to calculate a and b from the experimental values of the critical constants of the gas. It was in this way that the values of a and b used in the ethylene illustration in the last chapter we found. The relationships here are

$$a=\frac{27T_c^2}{p_c\times 273^2\times 64}; \quad b=\frac{T_c}{273\times 8p_c},$$

where in both expressions, for simplicity's sake we assume the value of the constant to be practically 1, in place of the very slightly larger value actually found (1.00643 for CO_2). If desired, of course, this could be included, raised to the second power, in the numerator, in the a value, and to the first power in the b expression.

If *in Van der Waals' equation we express the pressure, volume and temperature as fractions of their critical values*, i.e.,

$$T_r=\frac{T}{T_c}; \quad p_r=\frac{p}{p_c} \quad \text{and} \quad v_r=\frac{v}{v_c},$$

we find

$$\left(p_r+\frac{3}{v_r^2}\right)(3v_r-1)=8T_r.$$

These quantities with the subletter r are called *reduced quantities*, and the systems represented in this way are said to be in *corresponding states*. The reduced equation of state, as the above formula is called, is thus seen to be the same for all substances which are in corresponding states, for all "specific" values have disappeared from it. When systems are in corresponding states then, i.e., under corresponding conditions of temperature (at an equal fraction of the absolute critical, for example), we find that the reduced volumes of both liquid and gas (they would only be the same at the critical temperature), and the reduced vapor pressure are simply functions of the reduced temperature, i.e.,

$$v_r' = \frac{v'}{v_c} = f_1(T_r) = f_1\left(\frac{T}{T_c}\right)$$

$$v_r'' = \frac{v''}{v_c} = f_2(T_r) = f_2\left(\frac{T}{T_c}\right)$$

$$p_r = \frac{p}{p_c} = f_3(T_r) = f_3\left(\frac{T}{T_c}\right).$$

At equally reduced temperature (i.e., *at temperatures which are equal fractions of the critical temperature*) *the ratios* $\frac{\textit{volume of gas}}{\textit{critical volume}}$, $\frac{\textit{volume of liquid}}{\textit{critical volume}}$, *and* $\frac{\textit{pressure of saturated vapor}}{\textit{critical pressure}}$, *each have identical values, independent of the nature of the substance.* The values found in this way do not always agree satisfactorily with those of experiment, however, so it would appear that there is some point in the derivation which has probably been neglected.

As far as concerns vapor pressure, the boiling-point under atmospheric pressure should be a corresponding temperature; consequently the vapor pressures of two liquids equally removed from the boiling-point should be practically identical. In the case of ether and water this law seems to hold with considerable accuracy, but with many others the disagreements are comparatively large. If this law were true we should expect to find the ratio $\frac{T_{\text{b.p.}}}{T_c}$ constant for all liquids, and in fact we do find it fairly constant, having a value which varies slightly around 0.6.*

The critical temperature of a mixture of two liquids can be calculated in general by the formula,

$$t_{\text{mixt.}}=\frac{pt_1+(100-p)t_2}{100},$$

where p represents the percentage by weight of the liquid 1 and, naturally, $100-p$ that of the liquid 2. In other words, critical temperature is an *additive* property. (For further information on this subject, see Pawlewski, Ber., **15**, 460 and 2460, 1882, and Schmidt, Leib. Ann., **266**, 266, 1891, and for an exception to the general rule, see Kuenen, Phil. Mag., **40**, 173, 1895.)

When a solution of a solid substance is heated to its critical temperature it is observed that there is no separation of solvent and solute, so that apparently the gaseous solvent, under these conditions, has the same power to dissolve the substance that the liquid one had. (See Hannay and Hogarth, Chem. News, **40**, 256; **41**, 103, and Altschul, Zeit. f. comp. und flussig. Gase, **1**, 207. As to the possibility of the existence of the liquid above the critical temperature, see Bradley, Browne and Hale, Phys. Rev., **27**, 90–106.)

Vapor-pressure and boiling-point.—The vapor-pressure of a liquid is the pressure to which, at any fixed temperature, it will evaporate into an exhausted or other space. If the vapor thus formed is removed, naturally more vapor will form, and by successive removals of portions in this way the entire amount of liquid may be evaporated. To cause a liquid to evaporate continuously, then, it is necessary to remove the pressure of the vapor above it. This may be done as above, or the same condition may be attained by making the exhausted space large enough to contain the vapor of all the liquid and yet not reach a high enough pressure to prevent further evaporation. This latter condition is indeed obtained in the open air when the vapor-pressure of the liquid is increased to such an extent by heat that it exceeds the counter-pressure of the atmosphere. The temperature necessary for this is called the *boiling-point* of the liquid, *the boiling-point designating that temperature, at* ATMOSPHERIC PRESSURE, *at which liquid and gas can exist together in equilibium in all proportions.*

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* For a résumé of numerical data on critical temperatures and pressures, see Guye and Friedrich, Arch. sci. phys. nat., **9**, 505 (1900) and also Landolt, Börnstein, and Roth, Tabellen, 1912 edition, under critical constants.

Every external pressure corresponds to a certain temperature, and these two magnitudes increase and decrease together. At the critical temperature the significance of vapor-pressure is naturally lost. For every pressure under the critical one, however, there is a certain temperature at which gas and liquid may exist together in all proportions: this temperature is the boiling-point at that pressure. Correspondingly, for every temperature under the critical one, there is a certain pressure at which gas and liquid may exist in equilibrium in all proportions: this is the vapor-pressure at that temperature. Unless a boiling-point is directly determined at a pressure of 760 mm. then, it will be seen that it is always necessary to give the pressure as well as the temperature; for this is as important with the temperature, as a statement of the temperature is with the vapor pressure.

Although the boiling-point of a liquid has always been supposed to offer the best criterion as to its purity, Gutmann (Trans. Chem. Soc., **87**, 1037–1042, 1895, Jour. Am. Chem. Soc., **29**, 345–348, 1907, Stoltzenberg, Chem. Ztg., **34**, 66, 1910) has called attention to the fact that the freezing-point is a much surer indication, and proves it with results obtained with liquid air as the freezing mixture.*

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* See also in this connection the very recent work of Bridgeman, Phys. Rev., Feb. and Mar., 1914.

The vapor-pressure of a liquid may be determined in one of several ways. One method of theoretical interest which gives good results is by Walker. A current of dry air is passed through the liquid, which is held at constant temperature, and the loss in weight of the liquid observed. The air in passing through the liquid absorbs an amount of vapor proportional to the vapor-pressure of the liquid. If v_m is the volume of air which in passing through the liquid absorbs the weight of 1 mole, then in that volume we have the relation

$$pv_m = RT,$$

where p is the vapor pressure of the liquid at the temperature T, i.e., the *partial pressure* of the vapor in the air which has passed through.

If v_x is the volume of air which absorbs x grams of the liquid, with the molecular weight M *in the gaseous state*, then, we must have

$$pv_x = \frac{x}{M}RT,$$

or

$$p = \frac{x}{Mv_x}RT.$$

The term v_x here represents the total volume containing x grams of vapor, i.e., is that of air plus vapor; but that of the air itself may be taken as a rule, for the volume of the vapor is almost negligible in comparison with it.

It will be noted here that p, the partial vapor-pressure of the liquid, is a very important term, for the reason that only that amount of saturated vapor could exist in any space which would give this pressure; since any greater pressure would produce liquefaction down to that pressure, and any smaller pressure would be increased by the vapor pressure of the liquid present. Perhaps the clearest idea of this can be obtained when we attempt to find the volume occupied by 1 mole of the vapor given off by a liquid below its boiling-point. Thus water vapor at 25° C. cannot have a higher pressure than 23.76 mm., therefore the volume of 18 grams of saturated water vapor, on the assumption that the gas laws hold, would be at 25°,

$$v_m = 22.4 \times \frac{273+25}{273} \times \frac{760}{23.76} \text{ liters},$$

and only at the boiling-point could the pressure be 760 mm.

If, by aid of the pv_x formula, we compare two liquids at the same temperature, passing equal volumes of air through them, we find

$$\frac{p}{p'} = \frac{x}{M} \times \frac{M'}{x'},$$

or

$$p = \frac{p'xM'}{x'M},$$

where M and M' are the molecular weights of the substances in *gaseous* form, and the vapor pressure of one liquid is found in terms of the known one.

The equation may also be used, for one liquid alone, in its original form,

$$pv_x = \frac{x}{M}RT\cdot$$

but here we must assume that the saturated vapor behaves as a more permanent gas would, i.e., obeys the gas laws. The only difficulty in the *use* of this formula is *the necessity of having the same dimensions on either side*, which we have already noticed in considering the gaseous state. If p be expressed in atmospheres, v_x in liters and R in liter-atmospheres, little difficulty will be experienced. x and M are then found in grams, the ratio $\frac{x}{M}$ being equal to the number of moles going into the gaseous state. For further information on this valuable method, see Walker, Zeit. f. phys. Chem., 2, 602, 1888; Will and Bredig, Ber., **22**, 1084, 1889; Orndorff and Carrell, Jour. Phys. Chem., 1, 753, 1897; Perman, Proc. Roy. Soc., **72**, 72, 1903; Carveth and Fowler, J. Phys. Chem., **8**, 313, 1904; Berkeley and Hartley, Proc. Roy. Soc., **77**, 156, and **78**, 68, 1096; and Lincoln and Klein, Jour. Phys. Chem., 11, 318, 1907.

The greatest difficulty experienced in the experimental use of this method for vapor pressure, is that which is also observed in the attempt to find the boiling-point of a liquid, viz., the possibility of supersaturation. If we attempt to boil a liquid in a perfectly clean vessel, with no points or particles of foreign matter around which the bubbles can form, we find that the temperature rises considerably above the boiling-point, and yet no sign of ebullition appears.

If the liquid on the contrary contains a gas in solution, or any other liquid more volatile than it, or if air or steam is made to bubble through it, bubbles of the vapor will be formed, and the ebullition will be kept up by the evaporation of these bubbles at the surface. After long boiling which tends to remove the foreign substance, a later heating will cause any bubbles that are formed to adhere to the walls, until finally they collect in larger ones, and those on being released escape with almost explosive violence, and the liquid "bumps." It has been shown that drops of water can be heated to 180° C. and remain floating in a bath of a mixture of linseed oil and oil of cloves. Here the pressure of water vapor is 7514 mm. or nearly 100 atmospheres, and yet no boiling takes place.

To cause a liquid to boil at its real boiling temperature, i.e., to avoid superheating due to the supersaturation of vapor in the liquid, then, we usually place small pieces of a solid material with sharp edges in contact with it, as platinum tetrahedra are used in the Beckmann boiling-point apparatus, and thus offer as many points as possible on which small bubbles may form and be expelled.

Supersaturation phenomena are also observed in the converse process of a liquid forming from vapor. The formation of a cloud in vapor is often so sudden as to suggest that the condensation has first been retarded and then takes place instantaneously. It has been observed that the vapor pressure from the surfaces of small drops is higher than that from less curved surfaces. For this reason there could be little evaporation from the small drops, and deposition on the larger drops, until the pressure of the vapor around them had become more than saturated. Then, evaporation from the very minute and perhaps invisible drops would take place, with condensation upon the larger ones of smaller vapor-pressure, which would have the effect of increasing the size of the drops and the formation of a visible fog. Indeed, Aitken has shown that when ordinary moist air is cooled suddenly so as to form a fog, each particle is formed around a minute speck of foreign matter suspended as dust. When the air is nearly freed of dust by filtration through cotton wool, expansion of the vapor (i.e., the cooling produced by the external work done in expanding) produces a fine rain, consisting of comparatively few spheres of large diameter. By passing an electric spark from platinum points through the space we recharge the vapor with nuclei, so that instead of the rain, a dense fog of innumerable fine particles is produced by an expansion.

The heat of evaporation.—For the transformation of a liquid into its gaseous form, a considerable amount of heat is is necessary. There are two causes for this absorption of heat. The volume must be increased against atmospheric pressure, and the liquid must be transformed into the gaseous state. The former is of the smaller numerical value. Its amount, by definition, may be calculated from $pv_m = RT = 2T$ cals. (see p. 10); i.e., for every mole of water-vapor formed from liquid water, at 100°, $2\times(273+100)=746$ cals. are used for the expansion. Since the heat of evaporation of 1 mole (18 grams) of liquid water at 100° to steam at 100° is 9650 cals., and the amount necessary for the expansion is but 746 cals., it will be observed that the difference in energy-content of the two states, liquid and gaseous, is very considerable.

The ratio of the molecular heat of evaporation (=molecular weight *as a gas* multiplied by the heat of evaporation in calories per gram) to *the absolute boiling-point, at atmospheric pressure,* has been found experimentally by Trouton (Phil. Mag., (5), 18, 54, 1884) to be approximately constant for a very large number of substances, and equal in average to 21, i.e., $\frac{Ml}{T_{\text{b.p.}}}=21$. This means, as will be observed that *the molecular heat of evaporation of a liquid at its normal boiling-point, is proportional to the absolute boiling temperature.* Nernst has found this constant to vary with the temperature and has suggested two other forms * of the equation, which give satisfactory results for a large number of liquids. Later these equations were simplified by Bingham (Jour. Am. Chem. Soc., 28, 723–732, 1906) to the form

$$\frac{Ml}{T_{\text{b.p.}}}=17+0.011T_{\text{b.p.}}.$$

Although the substitution of the values of M, as a gas, l, and $T_{\text{b.p.}}$ in this equation shows that it holds for a very large number of substances, certain others give a greater value to the left side than to the right. This is interpreted as meaning that the substance as a liquid has a larger molecular weight than it has as a gas, i.e., is associated, and consequently requires an extra amount of energy, over that requisite for a simple evaporation, to perform the work of dis-association; and the difference in the values of the right and left sides is assumed to be an approximate measure of the amounts of the association. *When the substitution of the values of M, as a gas, l, and $T_{\text{b.p.}}$ gives the same value for the two sides of the equation, then, the substance is regarded as* NON-ASSOCIATED, *i.e., to have the same molecular weight in both the liquid and gaseous states; it is not possible, however, to calculate from the equation the extent of the association; when the two sides are not identical, in other words, we cannot solve for M and consider that the molecular weight as a liquid.*

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* $\frac{Ml}{T_{\text{b.p.}}}=9.5\log.T_{\text{b.p.}}-0.007T_{\text{b.p.}}$, and $\frac{Ml}{T_{\text{b.p.}}}=8.5\log.T_{\text{b.p.}}$. Gött. Nach., 1906.

It is to be remembered in this connection that the term M *refers to the gas*, so that the relationship does not allow us to solve for the molecular weight as a liquid. Association, however, would change the value of the normal latent heat of evaporation, for in addition to transforming liquid to gas, at the same temperature, *both having the same molecular weight*, we have also to transform the molecular weight of the liquid to that value it has as a gas. The relationship of Trouton, then, simply shows the abnormality of the value of l, as compared to a large number of substances which follow the law, *and we say this is due to the added work which is necessary to equalize the molecular weights, and therefore the liquid must have been associated.* If work is done by the dis-association, naturally l here would have a smaller value than it would normally. In both cases the heat involved in dis-associating the liquid would depend upon its nature.

It will be seen that this law is simply an extension of our "work" definition of molecular weight as a gas (p. 10); for the equation provides not only that the external work of formation of a mole of gas from negligible volume, but also the *total* *heat* of formation, is dependent with non-associated substances, *solely* upon the absolute temperature.

Tyrer (Proc. Chem. Soc., 27, 319) finds that the latent heat of a mixture of two normal liquids, when the heat absorbed by 1 gram of the mixture completely vaporizing at constant temperature is called l_m, also follows Trouton's law in the approximate form

$$\frac{l_m M_a}{T_{\text{b.p.}}} = \text{const.},$$

M_a being the average molecular weight of the mixture.

Another equation which can be used for the calculation of the heat of evaporation of *non-associated* liquids is given by Mills (Jour. Phys. Chem., 9, 402; 10, 1; 11, 132; 11, 154; Jour. Am. Chem. Soc., 31, 1099, 1909. See also Dieterici, Ann. d. Phys. (4), 25, 569, 1908) in the form $\dfrac{Mw - \text{ext. work}}{\sqrt[3]{d} - \sqrt[3]{D}} = \text{constant}$, where d is the density as a liquid, and D as a gas. This formula *can be used, and in that it differs from the Trouton-Bingham relation, at temperatures other than the boiling-point at atmospheric pressure.*

Still another equation, holding for non-associated liquids, has been derived by Crompton (Proc. Chem. Soc., 17, 61, 1901), as follows: Assume that the gas laws hold rigidly for a saturated vapor, and, further, that theoretically it is possible at constant temperature, and by compression alone to reduce the volume of a mole of gas, $v_m (= Mv_s)$, to that occupied by the liquid, $v_m' (= Mv_s')$,* without any change in state occurring and the gas continuing to obey the law throughout the compression. The work done in causing this change of volume will be equal, then, to

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* In this, instead of assuming the volume of the liquid as negligible (definition, p. 10), for the greater accuracy, we are to consider it. Here also there is no question of a *constant* pressure, as we assumed there. We shall represent the volume of 1 gram of liquid here by v_s', reserving v_s for use with gases only. Mv_s' we can therefore write v_m', when it refers to the liquid.

$$\int_{v_m'}^{v_m} pdv = \int_{v_m'}^{v_m} \frac{RT}{v} dv = RT \log_e \frac{v_m}{v_m'},$$

and as no change in temperature takes place, heat equivalent to this will be given out. The gas will now occupy the volume which would be occupied by the liquid, but of itself it will not retain its volume. In order to obtain it in such a state that it will do this it is necessary to remove its ability to expand. By removing a further amount of energy equal to that expended in compressing the material, viz., $RT \log_e \frac{v_m}{v_m'}$, we shall, however, also remove from it the power of expansion. The total heat given out, then, by the production of the liquid from the vapor, under these ideal conditions, must be $2RT \log_e \frac{v_m}{v_m'}$, and this is equal to the latent heat of evaporation of the molecular amount, i.e.,

$$L = Ml = 2RT \log_e \frac{v_m}{v_m'},$$

or, since the ratio of the molecular volumes $\frac{v_m}{v_m'}$ under normal conditions is the same as that of the specific volumes, or inversely as the specific densities, and using Briggs' logarithms, (0.4343 being the modulus), we have

$$L = Ml = 2RT \log \frac{v_s}{v_s'} \times \frac{1}{0.4343}.$$

Thus, since for CO_2 at $T = 248$, $d_l = 1.10$, $d_g = 0.044$, and $M = 44$, we find $l = 71.91$ calories, where the experimental value is 72.23.

This formula, which can also be used at any temperature, gives very accurate values at temperatures at which the vapor-pressure is high, but values which are too large for those temperatures giving low vapor-pressures; the divergence, at high vapor-pressures, being greater than one calorie only for a few cases (see Mills, l.c.). The term $\frac{Ml}{T_{\text{b.p.}}}$ of the law (p. 88) is equal, according to this equation, to $2R$ ($\log_e v_m - \log_e v_m'$), which for many liquids gives values lying between 22.8 and 23.9.

The heat of evaporation, however, also varies with the temperature. The expression for this variation is derived as follows: (1) Allow 1 mole of liquid to vaporize at the boiling temperature, T, against atmospheric pressure, and then heat this volume, holding it constant, to the temperature $T+\Delta T$. The gas in expanding has done the work $pv_m=RT$ and has absorbed the heat $Ms_v\Delta t$ in going to the higher temperature, while the latent heat of evaporation is L_T. (2) We reach the same final state by first heating the liquid to $T+\Delta T$, by which the heat $Ms\Delta t$ is absorbed, and then allow the gas to form at $T+\Delta T$, also against constant atmospheric pressure. The work of expansion here is $pv_m=R(T+\Delta T)$, and the latent heat $L_{T+\Delta T}$. By these two processes we have reached the same final state from the same initial one, so by the principle of the conservation of energy the amount of energy involved is the same in both cases. We have then

$$-RT+L_T+Ms_v\Delta T=-R(T+\Delta T)+Ms\Delta T+L_{T+\Delta T}$$

$$R+Ms_v-Ms=\frac{L_{T+\Delta T}-L_T}{\Delta T},$$

and since, according to page 55,

$$Ms_v+R=Ms_p,$$

$$Ms_p-Ms=\frac{L_{T+\Delta T}-L_T}{\Delta T}=\frac{\Delta L}{\Delta T},$$

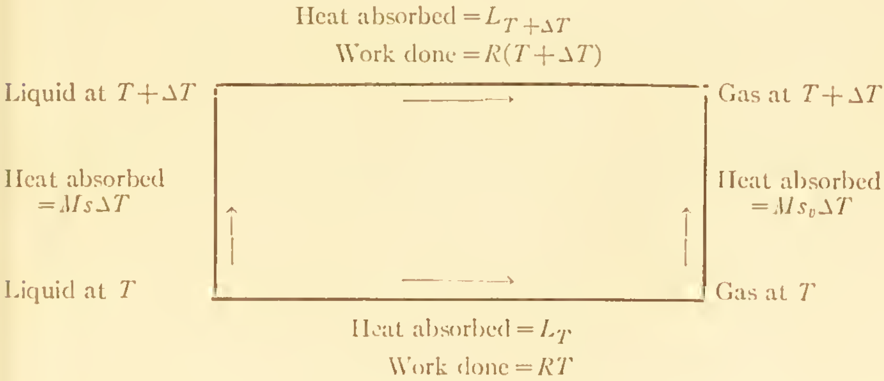
or

$$s_p-s=\frac{\Delta l}{\Delta T},$$

i.e., *the latent heat of evaporation, in the neighborhood of any temperature, increases per degree by an amount equal to the specific heat of the gaseous state at constant pressure, minus the specific heat of the liquid, both at that temperature.* Since the specific heat of the gas is always less than that of the liquid, this increase is always negative, i.e., the heat of evaporation always decreases with increasing temperature. s for benzene at 50° is 0.45, s_p for 50° (see p. 59) = 0.295, hence the temperature coefficient of the heat of evaporation of benzene around 50° is -0.155 cal. per degree, for $\frac{\Delta l}{\Delta T} = 0.295 - 0.45 = -0.155$; where the value -0.158 has been found by experiment, the difference being within the experimental error.

In the derivation of this equation we have used $pv_m = RT$, hence we can only expect it to hold rigidly when the simple gas laws themselves hold.

This derivation, perhaps, will be clearer from a consideration of the accompanying diagram, which shows each change, together with the energy differences of the changes.


Heat absorbed $= L_{T+\Delta T}$
Work done $= R(T+\Delta T)$
Liquid at $T+\Delta T$
Gas at $T+\Delta T$
Heat absorbed $= Ms\Delta T$
Heat absorbed $= Ms_v\Delta T$
Liquid at T
Gas at T
Heat absorbed $= L_T$
Work done $= RT$

The relation between vapor-pressure, heat of evaporation, and temperature. An equation showing the relation between these three quantities can be found as follows: Start with 1 gram of liquid at T, and under its own vapor-pressure p. Heat

ΔT° and assume it to be completely transformed into gas. During this process heat equal to $l_{T+\Delta T}$ will be absorbed at the temperature $T+\Delta T$, the volume will change from v_s' to v_s, and the vapor-pressure from p to $p+\Delta p$, while work equivalent to $(v_s-v_s')(p+\Delta p)$ will be expended.

Now cool this vapor to T° and allow it to condense, under the pressure p, to its original volume v_s'. The change in volume will be the same as before, with the opposite sign, but the heat evolved, l_T, will be smaller than the amount absorbed, $l_{T+\Delta T}$, for some of the heat has been transformed into work. The work gained by the system during this process at T will be only $p(v_s-v_s')$. The total work done by the system, then, is $(p+\Delta p)(v_s-v_s')-p(v_s-v_s')$, i.e., $\Delta p(v_s-v_s')$.

Since l (the latent heat of evaporation at T, i.e., l_T) is the heat available at T, and the work $\Delta p(v_s-v_s')$ has been done by the transformation of heat into work, we have (p. 56),

$$\frac{\Delta p(v_s-v_s')}{l}=\frac{\Delta T}{T},$$

i.e.,

$$\frac{l}{T(v_s-v_s')}=\frac{\Delta p}{\Delta T}, \quad \text{or} \quad \frac{T(v_s-v_s')}{l}=\frac{\Delta T}{\Delta p}.$$

Dropping the negligible volume v_s' and assuming the vapor to behave as an ideal gas, we would have, since

$$p(Mv_s)=RT, \quad \text{or} \quad v_s=\frac{RT}{pM},$$

$$\frac{\Delta p}{\Delta T}=\frac{pMl}{2T^2},$$

or

$$\frac{\Delta T}{\Delta p}=\frac{2T^2}{pMl}.$$

It must be remembered that the latter forms are derived on the assumption of ideal conditions, and will depend in accuracy upon the holding of these conditions. The first two, on the other hand, are independent of the holding or non-holding of the gas laws.

We find thus that the change in vapor-pressure (in atmospheres) of a liquid per degree is equal to the heat of evaporation (in liter atmospheres) per gram of the liquid, divided by T times the change in volume (in liters); or the change in boiling-point per atmosphere is equal to T times the change in volume in liters, over the heat of evaporation per gram, expressed in liter atmospheres.

The equation of which these are but various forms is called the *Clapeyron-Clausius equation*, and it can be safely assumed to hold rigidly, except when the gas laws are later applied to it (the second set of equations), when its accuracy will be only equal to that of these laws.

It will be observed here that in the term giving the difference in volumes, the volume of the system containing the *greater* amount of energy at the same temperature (the gaseous) always comes *first*, the volume of the system containing the smaller amount of energy (the liquid) being subtracted from it.

It is necessary to remember in using these equations that $2 (=R)$ and l are in calories and p in mechanical units, while $\frac{\Delta p}{\Delta T}$ gives us that change in vapor-pressure for 1° of temperature, $\frac{\Delta T}{\Delta p}$ giving the change in boiling-point per unit of external pressure. To get a correct result, then, care must be taken with the dimensions. It is safest, with the first two equations, always to express the pressures as atmospheres, the volumes in liters, and l in liter-atmospheres, afterwards transforming the result into the units desired.

Example.—The boiling-point of ethyl iodid at 73.3 cms.

is 72°.2 C., $Ml=7597$; find change in vapor-pressure for 1° C. We have

$$\frac{\Delta p}{\Delta T}=\frac{pMl}{2T^2}=\frac{7597\times 73.3}{2\times(345.5)^2}=2.34 \text{ cms. Hg.}$$

In this form of the equation there can be no trouble with the dimensions, for we have calories in both numerator and denominator, so that the units used for p will be those of the result $\frac{\Delta p}{\Delta T}$, i.e., the change in pressure per degree.

An example of the more accurate form is the following. At 80° C. the saturated vapor-pressure of ethyl acetate is 832.7 mm. Find the boiling-point of the liquid under atmospheric pressure. $v_s'=1.213$ and $v_s=285$ cc., $l_{80}=85.5$ cals. Here we have

$$\frac{\Delta p}{\Delta T}=\frac{w}{T(v_s-v_s')}=\frac{85.5\times 0.041}{353(0.285-0.0012)},$$

when we transform the calories into liter-atmospheres by multiplication by 0.041 (since $R=2$ cals. $=0.08204$ liter atmospheres), and the cc. into liters. Solving the above we find the change in vapor-pressure, in atmospheres per degree, and, by multiplication by 760, find $\frac{\Delta p}{\Delta T}=26.6$ mm./degrees. Since we must find the temperature corresponding to 760 mm., i.e., a change of 72.7 mm., division of that by 26.6 leads to 2°.73, and this subtracted from 80° gives us as the boiling-point under atmospheric pressure 77°.27, whereas 77°.2 is observed experimentally.

A general and simple, and naturally more approximate formula, which can be used in place of the Clapeyron-Clausius equation is

$$\frac{\Delta p}{\Delta T}=\frac{8500}{T_{\text{b.p.}}} \text{ mm./degrees} \quad \text{for non-associated liquids,}$$

and

$$\frac{\Delta p}{\Delta T}=\frac{10{,}200}{T_{\text{b.p.}}} \text{ mm/degrees for associated liquids,}$$

the first being used for what we have called normal, non-associated, liquids; the second for associated ones.

These equations, which are only fitted for use where some of the data necessary in the others is missing, can be derived from the relation of Trouton $\left(\frac{Ml}{T_{\text{b.p.}}}=\text{const.}\right)$ and the Clapeyron-Clausius equation. For water, an associated liquid, for example, we find $\frac{\Delta p}{\Delta T}=26.5$, while experiment gives 27.1 mm. per degree.

Refraction of light.—La Place, in determining the velocity of light in various media, found the relation,

$$\frac{n^2-1}{d}=\text{constant for all temperatures,}$$

where n is the refractive index of the liquid and d is the density of the medium. For many liquids this holds true, approximately, but Gladstone and Dale found empirically a relation which holds more exactly and for many more liquids than the former. This is

$$\frac{n-1}{d}=\text{constant for any one liquid.}$$

Further, in the case of a mixture, the constant in this form is found to be equal to the sum of those for the ingredients. We have then

$$p\frac{n-1}{d}=p_1\frac{n_1-1}{d_1}+p_2\frac{n_2-1}{d_2},$$

where p is equal to 100, and p_1 and p_2 represents the percentages by weight of the two ingredients. By aid of this it is possible to make an optical analysis.

Example.—An unknown mixture of amyl and ethyl alcohols gives $n=1.3822$, $d=0.8065$. What is the percentage composition of each in the mixture?

For amyl alcohol $n_1=1.4057$, $d_1=0.8135$; for ethyl alcohol $n_2=1.3606$, $d_2=0.811$; hence

$$100\times 0.4738=p_1\times 0.4987+p_2\times 0.4501;$$

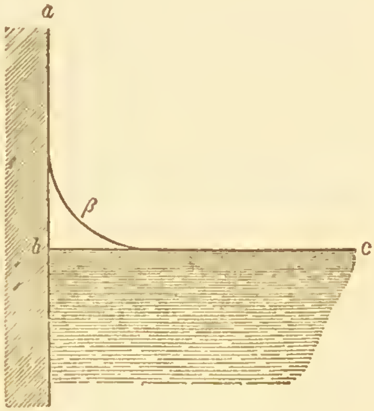
and since $p_1+p_2=100$, we find $p_1=48.8$, $p_2=51.2$. By direct weighing it was found that p_1 is 48.9 and p_2 is 51.1.

This formula also holds approximately for solutions, i.e., for finding the coefficient of refraction in the solid state from that of the solution and the solvent. For other illustrations of this method see Mayberry and Shepherd (Am. Chem. Jour. **29**, 274, 1913).

Surface-tension.—*The surface-tension γ of a liquid is the force acting on the unit of length (1 cm.) of its surface.* The work (per square centimeter) of formation of a surface of definite size, therefore, is equal to the product of the surface tension into the area of that surface—and the value of the surface work per square centimeter is equal *numerically* to that of the surface tension per centimeter.

It is clear from this that any experimental method for the measurement of the surface work performed by any liquid gives us a method for the estimation of its surface tension. A surface of liquid is thus seen to behave as a stretched sheet of india-rubber, and exerts a tension of the same sort, except that, unlike the rubber, its tension is constant, and does not depend upon the amount of the stretching. This is the property of a liquid which causes it to rise in a capillary tube, for, by it, the surface of the liquid formed in the bore of the tube will continuously decrease in size, raising liquid with it, until the weight of the column of liquid becomes equal to the surface tension for the length of contact; when the surface will remain at rest, and the column will remain constant in height.

Some liquids wet glass, while others do not, and upon this depends the shape of the surface formed. Imagine a plate of glass suspended vertically in a vessel of water, i.e., a liquid which wets the glass. The glass will then be wet as high as *a* (Figure) and the surface *abc*, owing to its surface tension, will decrease in size by assuming the shape *aβc*. In doing this a certain weight of liquid will be raised. When the weight *w* of this portion raised is equal to the surface-tension for that length of surface, *l*, equilibrium will be established, i.e.,



$$l\gamma = w$$

or

$$\gamma = \frac{w}{l}.$$

If now instead of using a plate we use a capillary tube, with a bore-radius equal to r, l will become $2\pi r$; and the weight of liquid raised in the tube will be

$$w = \pi r^2 hd,$$

where h is the height of ascension of the liquid in the tube (measured downward in case the liquid does not wet the walls), and d is the specific gravity of the liquid. We have then, substituting these values for w and l above, and assuming that the angle of contact of liquid and glass is zero (an assumption apparently justified by experiment),

$$\gamma = \tfrac{1}{2}(hrd),$$

or, when h and r are expressed in centimeters, since d is equal to the weight in grams of 1 cc. and g to 980.1,

$$\gamma = \tfrac{1}{2}(hrd)980.1 \text{ dynes per centimeter},$$

i.e., *the surface-tension of a liquid can be calculated directly from its specific gravity and the height to which it ascends in a capillary tube of the radius r.*

Surface tension is usually expressed thus in dynes per centimeter; and surface work, consequently, in ergs per square centimeter.

Another expression derived from the height of ascension of a liquid in a capillary tube is the so-called "*specific cohesion*," which is defined as *the height in millimeters to which a liquid would rise in a capillary tube of a radius of 1 millimeter*, and which is equal, in short, to the product of the height of ascension in any tube into the radius, both in millimeters. This quantity is usually designated by the symbol a^2; we have, therefore,

$$a^2 = h'r';$$

or, since $h'r'$, both in millimeters, equals 100 hr, where both are in centimeters,

$$a^2 = \frac{2\gamma}{9.80d}$$

This method for determining surface-tension or specific cohesion is the only accurate experimental means we have at present which gives *absolute* results. But there are numerous others which enable us to find the *relative* value of these quantities, *provided the method is first standardized by aid of a liquid for which the absolute values are known.* One of the most accurate of these, and at the same time one of the most simple to use is that based upon the weight of a falling drop as proposed by Tate (Phil. Mag. (4), **27**, 176, 1864), and since corroborated, *in a restricted form*, very completely by the experimental work of Morgan and his co-workers.*

Owing to the elastic nature of the surface of a liquid in contact with air or a gas, small free portions of liquid always assume that shape which insures the smallest possible surface, viz., the spherical form. That the drops of rain, as produced by the sudden condensation of water vapor, are perfectly spherical is shown by the perfect circularity and definiteness of the rainbow. For the same reason a liquid wetting a stirring rod collects at the lower portion of the rod when it is removed from the liquid, and forms a drop. If the weight of this drop is greater than the tension of the elastic surface separating the liquid from the air the drop must then fall, while the portion remaining assumes a shape which for that weight of liquid *on that area* is the smallest possible—naturally here, however, the remaining drop would only be hemispherical on one definite area of rod surface.

A drop of liquid formed on the outer edge of a capillary tube, the liquid being supplied very gradually through the bore, should break off, then, and fall when the weight of the drop just exceeds the surface tension of the liquid for the length of the line of contact at which the drop breaks away from the mass of liquid. This separation never seems to take place at the glass edge itself, however, but always from the neck of liquid formed by the constriction of the drop before it falls—in fact the phenomenon is similar to that which is observed when a thin rubber balloon, attached to a wire ring, is gradually filled with water, for the lower portion of the bag fills out into a more or less spherical mass just before the rubber ruptures, not at the ring, but at a place just below it which has a smaller diameter than the ring. For this reason, it is impossible for us to calculate the absolute value of the surface-tension of a liquid from the weight of the drop falling from a tip of a definite diameter, for the *real diameter from which the drop actually falls* is smaller than that, and is not directly measurable. Experiment shows, however, that while the liquid never separates as a drop from the glass itself; *it does separate from the mass of liquid for tips lying between certain definite limits, from a diameter that stands in a definite numerical ratio to that—and which is the same, from the same tip, for all liquids, and is proportional to the diameter, when various tips, within these limits, are employed.* In this case, then, we have, simply, surface-tension = constant × drop weight, from any one such tip.

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* Jour. Am. Chem. Soc., Vols. **30**, **33** and **35**. See also for a résumé of all the work, Zeit. f. phys. Chem., 1914.

Of these two methods for the determination of surface tension, the one by capillary rise gives *absolute* values, while that by aid of the weight of the falling drop gives *relative* ones; for the tip must first be standardized, i.e., the value of its constant determined by aid of benzene, for example. The method is especially valuable, however, because it enables us to keep the error constant, no matter what the magnitude of the drop; for if this is small a larger number of drops can be weighed, and the weight of one calculated from this weight. In the capillary rise method, on the other hand, the smaller the value of surface-tension, the smaller the height of ascension, and the greater the error in measuring it. The temperature coefficient of surface-tension thus should be determinable with greater precision by aid of drop weight than by capillary rise.

In closing this section on surface-tension, it will be of interest perhaps to note the effects attributable to the action of surface-tension in various physical phenomena. That the surface film of a liquid is really elastic, as we have assumed above, is perhaps best proven by the careful placing of a fine needle upon the surface of water, when it is observed to float and stretch the surface of the liquid, causing a depression to be formed in it, but without rupturing it. A reason for the existence of this elastic film is apparent when we consider that every portion of the liquid in the interior will be attracted equally on all sides, while the surface portion, i.e., on a boundary surface, will only be attracted by the cohesive force of the mass of liquid below it—so that a surface *should* exhibit a force which tends to resist any attempt to break it.

The visible effect due to a change in the surface tension of a liquid by the addition of another liquid to it is clearly shown by placing a drop of alcohol colored with some dye, insoluble in water, upon a layer of water on a glass plate. Here alcohol dissolves in the water surrounding the drop and the surface-tension of water is depressed in the solution formed, so that the surface contracts and pulls away from the alcohol, leaving a dry space surrounding the drop. The effect of the addition of substance to water, as far as a change in its surface tension is concerned, is best illustrated perhaps when the added substance is amyl alcohol. It is thus found (Jour. Am. Chem. Soc., 35, 1863, 1913) that at 30°, 0.25% of amyl alcohol in water depresses the surface-tension of the latter from 71.03 to 53.7 dynes or by nearly 25%; 0.5% produces a change of nearly 38%, 0.75% gives 42%, 1% one of 47%, while a saturated solution (about 2.5%) lowers the surface-tension by 64%.

The effect of added substance to a liquid is not *always* a depression of the surface-tension, however, for many cases are known where the surface tension is increased. It is natural here to assume, though, that if no chemical reaction takes place between the liquids, the surface-tension would be additive, i.e., the total surface-tension would be equal to the summation of the surface-tensions of the constituents, each multiplied by the percentage to which it is present in the mixture—and such cases are known.

Valson (Compt. rend., **74**, 103, 1872) has endeavored to prove in the case of dissolved salts that all aqueous solution containing the same number of equivalents have identical surface-tensions, but no one has been able to corroborate his results, and, in fact it has been shown by later work (Jour. Am. Chem. Soc., **35**, 1750, 1759, 1913) to be entirely without foundation; although in the case of very concentrated solutions (ibid., 1845) it appears that the surface-tension per equivalent of salt is more nearly equal for various solutions than is the surface-tension per gram—in other words, that the law might be regarded there as a very rough approximation.

The vapor-pressure of a large surface of pure liquid depends only upon its nature and temperature, as has already been made clear, but with a fixed temperature it has been found to vary also with the curvature of the surface of the liquid; the more convex outward the surface, the greater the vapor-pressure. It is for this reason that small drops of water in a cloud evaporate; the vapor afterwards condensing on the larger drops, which exhibit a lower vapor-pressure. On the same principle is the experiment of Sir W. Thomson (Roy. Soc. Edin., 1870) where in a space under the vapor-pressure only of the liquid, a distillation was observed from a plane liquid surface to the concave meniscus in a capillary tube. Naturally, this difference in vapor-pressure here is not very large, though of course, it need not be for a distillation to take place; *any* difference accounting for that. Calculation shows that with a capillary tube of an internal radius equal to 0.001 mm. the difference in vapor-pressure of water at the plane surface and at the meniscus would be one-thousandth of the value of the vapor-pressure itself; in other words, the vapor-pressure at the meniscus would be 0.999 of the vapor-pressure of water at the plane surface.

The surface-tension of water is the highest known among pure liquids (though some strong aqueous solutions, $CaCl_2$ for example, have a much higher value), so it is very difficult to retain its surface in a pure state, as so many substances tend to lower its value. A more striking effect visually of the lowering of the surface-tension of water by dissolved substances than the one with amyl alcohol cited above is the following. When small fragments of camphor are scraped off with a knife and allowed to fall upon the surface of pure water, they at once assume vigorous movements, principally of rotation. But if the surface be touched with the finger the motion will cease owing to the grease communicated to the water. These movements are due to the gradual solution of the camphor, and to the fact that the solution formed has a smaller surface-tension than the water. For this reason, the portion of the surface immediately surrounding the fragment is continually being drawn outward away from the fragment. If the dissolving were uniform the fragments would remain at rest; but owing to the irregular outline of the fragments and the different speed of solution, the tension on the surface is not the same on all sides, and the differences set the small fragments in rotation.

There is a decided difference between the mechanical behavior of clean and contaminated surfaces. In the former, no force opposes the expansion of one part and a contraction of another. A film of grease on the surface, however, increases the thickness of the surface layer on contraction, and decreases it on expansion. These differences of thickness entail corresponding differences of tension, so that in such a greasy surface there are forces always tending to restore the original undistorted condition. This is the explanation offered by Reynolds (Proc. Roy. Soc., 48, 127) for the effect of oil upon waves—for the production of waves imposes upon the surface local expansions and contractions, to which the greasy surface offers opposition.

In this behavior the surface of water when covered with a film of oil differs from a pure liquid, whose surface-tension is independent of its state, in that, like stretched rubber, its tension depends upon the extent of the stretching.

A homely illustration of the effect of surface-tension is given by the removal of a grease spot from cloth by the application of gasolene. The fatty oils here have a greater surface-tension than the solvent, so that the solution formed is attracted from the solvent toward the grease (just as the solution of camphor in water was attracted away from the solid). If in order to cleanse the grease spot we wet it with the solvent, we simply drive away the grease to the clean portion of the cloth. The solvent should therefore be applied first in a ring around the spot, and gradually brought nearer the center, while blotting paper should be placed in contact with the cloth so that when the grease is finally driven in this way to the middle of the spot, it may be absorbed, instead of remaining as globules on the surface, to return to the cloth on the evaporation of the solvent. Since the surface tension of a liquid always decreases with increased temperature, the application of heat, causing the temperature to be different in different parts of a greasy surface, causes the grease to go toward the cooler portions. The application of a hot iron to one side of the cloth and blotting paper to the other thus causes the grease to be driven into the blotting paper.*

If a particle were removed from the center of the liquid where it is attracted in all directions equally, to the surface, where the attraction is only downward, as Stefan (Wied. Ann., **29**, 655, 1886) has pointed out, the force of attraction or of cohesion in a liquid, its *normal pressure*, as it is called, must be equal to twice its latent heat of evaporation, since the work of carrying liquid from the surface to the gaseous state has only to overcome one-half the force necessary to bring it from the interior to the surface, and then transform it to gas from that.

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* For these illustrations of surface tension I am much indebted to Maxwell, Theory of Heat, 10th ed., 281–301.

That this normal pressure of a liquid must be very great can be imagined after examining the cohesive pressures $\frac{a}{v^2}$ given in the tables under the application of the equation of Van der Waals.

Surface-tension, molecular weight and critical temperature.—The surface-tension of a liquid has been found to depend upon the temperature and nature of the liquid, and is the basis of two definitions of molecular weight in the liquid state. The first connection between surface-tension and molecular weight was found by Eötvös (Wied. Ann., **27**, 448, 1886), who observed experimentally that the surface-tension multiplied by the $\frac{2}{3}$ power of the product of molecular weight and specific volume, is a function of the absolute temperature. This relation, expressed mathematically, is

$$\gamma(Mv_s')^{\frac{2}{3}}=f(T),$$

where γ is the surface-tension in dynes, M the molecular weight, and v_s' is the specific volume, i.e., the reciprocal of the density, of the liquid. Ramsay and Shields (Zeit. f. phys. Chem., **12**, 431–475, 1893) expressed this relation in the form

$$\gamma v_m'^{\frac{2}{3}}=\gamma(Mv_s')^{\frac{2}{3}}=k(\tau-6),$$

where τ is the temperature, reckoned downwards from the critical one, i.e., is equal to t_c-t_0, where t_c is the critical temperature and t_0 the temperature of observation, at which both the γ and v_s' values hold, and k is a constant independent of the nature of the liquid. τ here, however, must always be greater than 35 for good results.

Ostwald explains the relation as follows: If the liquid mole were in spherical form, its surface would be proportional to the volume raised to the $\frac{2}{3}$ power, since

$$v'_{m,1} : v'_{m,2} :: r_1^3 : r_2^3, \text{ and surface}_1 : \text{surface}_2 :: r_1^2 : r_2^2.$$

We see, then, that the above law simply expresses the fact that the work necessary to form the molecular surface depends only upon the temperature, as calculated downwards from the critical one (or at least a point about 6° below this), at which the surface-tension and the work are both equal to zero; for the meniscus at this point disappears. The law, in fact, is exactly analogous to the gas law $pv_m = RT$, for in this at the point from which T is reckoned (upward) the volume of the gas is equal to zero, and the volume and work above that temperature depend only on the temperature, and are independent of the nature of the gas.

Using as M the value observed in the gaseous state, Ramsay and Shields found k for many liquids to be equal to approximately 2.12 ergs. These liquids included benzene, chlorbenzene, ether, phosphorus trichloride, and many others.

An example of the use of this Ramsay and Shields equation for a normal liquid will perhaps make it clearer. The radius of a capillary tube is 0.01843 cm., at 46°, h (the height of CCl_4 in the tube) $= 1.643$ cm., d (the density) $= 1.5420$, hence $\gamma = \frac{1}{2} hrd \times 980 = 22.9$ dynes per centimeter. Since the critical temperature is 284°, k is 2.12, and $\gamma(Mv_s')^{\frac{2}{3}}$ is 491.8, M is found to be 153.7; as against the value 153.8 from the formula, CCl_4.

Ramsay and Shields proposed to define the molecular weight in the liquid state in terms of this equation, in such a way that *the molecular weight of a liquid at any temperature is that weight in grams which at that temperature will occupy such a volume* Mv_s' *(in cc.), in the formula* $\gamma(Mv_s')^{\frac{2}{3}} = k(\tau - 6)$, *that* k *is equal* *approximately to 2.12 ergs, when γ is expressed in dynes.* For this purpose it is necessary, of course, to know the surface-tension at that temperature and the term τ, i.e., the difference between the critical temperature of the liquid and the temperature of the experiment. As it is not an easy matter to determine the critical temperature experimentally this definition is not very convenient, but they suggested that it is possible to rearrange it in such a way that the knowledge of the critical temperature is not only unnecessary for the calculation of the molecular weight, but that it, also, may be calculated from it. If the surface-tensions and specific volumes (or densities) of any one liquid are known at two temperatures, for example, we would have, using the reciprocal of the density in place of the specific volume, and t_c-t in place of τ,

$$\gamma_1\left(\frac{M}{d_1}\right)^{\frac{2}{3}}=k(t_c-t_1-6), \quad \text{and} \quad \gamma_2\left(\frac{M}{d_2}\right)^{\frac{2}{3}}=k(t_c-t_2-6);$$

and by subtracting the second from the first we would obtain

$$\frac{\gamma_1\left(\frac{M}{d_1}\right)^{\frac{2}{3}}-\gamma_2\left(\frac{M}{d_2}\right)^{\frac{2}{3}}}{t_2-t_1}=k=2.12 \text{ ergs},$$

for $(t_c-t_1)-(t_c-t_2)$ is equal to t_2-t_1, the difference in the temperatures of observation.

This equation, however, simply expresses the fact that *the temperature coefficient of the molecular surface-tension for all liquids is approximately 2.12 ergs.* According to this, then, *the molecular weight in the liquid state is that weight in grams which at that temperature gives such a volume that a change in temperature of 1° involves an amount of surface-work, according to the above formula, equal to approximately 2.12 ergs.* This is similar to a definition which might be used for the gaseous state, i.e., the one expressive of the amount of external work involved by the change in temperature of 1 mole of gas 1°. This work, according to p. 10, is equal to *R*, and we may say the molecular weight in the gaseous state is that weight in grams occupying such a volume that a temperature-change of 1° will involve the external work *R*, i.e., 2 calories, 0.08204 liter-atmospheres, or 8.31×10^7 ergs.

In this way it would seem that we have found a definition of molecular weight as a liquid, in which a knowledge of the critical temperature is unnecessary.

Knowing that *M*, as a liquid, is the same as it is as a gas; in other words, knowing *k* to be constant and independent of the temperature, even though its value is not exactly the same as the average approximate value of *k*, viz., 2.12, Ramsay and Shields also suggested the possibility of calculating the critical temperature by aid of the original equation. In order that the correct value of the critical temperature may be obtained from these values, they found it necessary to use the exact, specific, value of *k* holding for the liquid in question. An example of the whole calculation will perhaps make this clearer.

At 19°.4, for CS_2, $\gamma=33.58$, at 46°.1, $\gamma=29.41$ dynes. We have then for $\gamma(Mv_s')^{\frac{2}{3}}$ at the two temperatures

$$\left(\frac{76}{1.264}\right)^{\frac{2}{3}} \times 33.58 = 515.4 \quad \text{and} \quad \left(\frac{76}{1.223}\right)^{\frac{2}{3}} \times 29.41 = 461.4.$$

Where 1.264 and 1.223 are the densities at the two temperatures, $\frac{\Delta(\gamma(Mv)^{\frac{2}{3}})}{\Delta t}$, i.e., $\frac{\gamma_1\left(\frac{M}{d_1}\right)^{\frac{2}{3}} - \gamma_2\left(\frac{M}{d_2}\right)^{\frac{2}{3}}}{t_1 - t_2} = k$, is then equal to $\frac{515.4 - 461.4}{46.1 - 19.4} = \frac{54.0}{26.7} = 2.022$, which is the specific value of *k* in this case. The critical temperature of CS_2 is then equal to $\frac{515.4}{2.022}+6+19.4=280^\circ.3$ C., (or to $\frac{461.4}{2.022}+6+46.1$) as compared to the experimental one of from 273° to 279°.6.

It will be seen from the above that the original Ramsay and Shields equation is simply an extrapolation to find, from the change per degree, the temperature at which the molecular surface-tension would become zero; for it must become that at the critical temperature (or 6° below it), as at that point the liquid and gas are indistinguishable, and the liquid does not form a visible surface.

For a large number of liquids Ramsay and Shields found values of k from the differential equation which were approximately 2.12, but which varied around that by from 1 to 10%; but notwithstanding this they designated these liquids as normal or non-associated. With respect to the calculated critical temperatures, later work has shown the method also to be unsatisfactory, the agreement in some few cases being good, while in very many others differences as high as 50° or more were noted. *In short by this method we find that the k values calculated from experiment vary widely from 2.12, and, further, that the critical temperatures so calculated do not agree in general with those found by direct experiment.*

All the above refers to what Ramsay and Shields designate as normal or non-associated liquids. There is a large class of liquids, however, for which the relation does not hold at all, viz., those for which the value of k as calculated by aid of the differential equation $\frac{\Delta\left[\gamma\left(\frac{M}{d}\right)^{\frac{2}{3}}\right]}{\Delta t}=k$ varies with the temperature, always increasing with increased temperature. Ramsay and Shields in this case regarded the liquid as associated, the association breaking down with increasing temperature, and giving a value of k which increased toward the normal k value as a limit, viz., 2.12. In order to find what molecular weight would be required, if the equation for normal liquids was to hold for this, they then wrote the equation in the form

$$\frac{\Delta}{\Delta t}\left[\gamma\left(\frac{xM}{d}\right)^{\frac{2}{3}}\right]=2.12,$$

from which, if

$$\frac{\Delta}{\Delta t}\left[\gamma\left(\frac{M}{d}\right)^{\frac{2}{3}}\right]=K,$$

K being the specific value found when using as M the gaseous molecular weight, they concluded that

$$x=\left(\frac{2.12}{K}\right)^{\frac{3}{2}},$$

where x is the factor of association, i.e., *the number of gaseous, molecular weights in one liquid molecular weight* in the temperature region in question. An example of this for water taken from their work is as follows: K around 10° (i.e., between 0° and 20°) is 0.87, hence $x=3.81$, i.e., the association of liquid water at 10° is such that its molecular weight is 3.81×18, in place of the gaseous value 18.

The fundamental weakness in the reasoning of Ramsay and Shields here, and unfortunately the same can be said of all other methods for the calculation of the extent of the abnormality of the molecular weight in the liquid state, is that no liquid has yet been found for which the value of K, which always approaches the normal value 2.12, ever attains it; so they assume the only change in the equation necessary for such a case to be one in the molecular weight; whereas such liquids may never be intended, so to speak, to follow the law at all.

It will be remembered from the discussion of the gaseous state, that in addition to those gases which follow the definition of normal molecular weight, as expressed in terms of volume, we also found gases that gave normal values at some temperatures, and then gradually dissociated, showing increasing abnormality with increased temperature. In such a case, naturally, we are justified in determining the molecular weight by aid of the density, and if the value found is not normal, ascribing it to dissociation, for such changes can be followed in other ways; and we know our method holds both when the system is normal and when it is abnormal, since with the same substance we find normal conditions at one temperature, and abnormal values at others. If in the case of liquids we could only find a similar state of affairs, and obtain a law holding for the liquid, and then under other conditions failing to hold for the same liquid, we should be on solid ground. But no such liquid is known, and until it is found the attempted calculation of the factor of association by such a relationship must be futile.

We see thus that the résumé of the work of Ramsay and Shields shows it to be unsatisfactory both from the point of view of the constancy of k for normal liquids, and for the calculation of the critical temperature; as well, in addition, for the purpose of estimating the extent of association, if that process really exists.

Morgan (Jour. Am. Chem. Soc., 33, 643, 1911) has called attention to the fact that the variable values of k as found by the differential equation of Ramsay and Shields are really due to the multiplication of the experimental errors inherent in any equation of this form. Thus in the illustration of CS_2 given above, errors of 0.1 of one per cent in opposite directions in the values of surface-tension—an error which is practically impossible to avoid even at best in capillary rise measurements—would produce a much magnified error in the value of k calculated from them. Thus an error of less than 0.1 of one per cent in the two values of $\gamma\left(\frac{M}{d}\right)^{\frac{2}{3}}$ on page 110 would give 515.9 and 461.0, in place of 515.4 and 461.4, and would thus lead to $k = \frac{54.9}{26.7} = 2.056$, in place of 2.022, i.e., an error of 1.7% in k, due to two errors of 0.1 of one per cent in the experimental quantities. These differences are often much larger than this, and are increased also in the same way by the same kind of an error in the denominator, due to the errors in the readings of the individual temperatures; for in all such cases the error in the two results themselves is carried over bodily to the difference between them, which is very much smaller than they, so that the percentage error is correspondingly magnified. This fault is of course fatal to the method, and the definition of normal molecular weight as a liquid can only be very approximate at best, if based upon such a relation.

An empirical definition of *normal* molecular weight in the liquid state, depending upon the surface tension, which has been proposed by Morgan (Jour. Am. Chem. Soc., 33, 643, 1911; see also Zeit. f. phys. Chem., 1914) has the advantage that it shows that the temperature coefficient of the Ramsay and Shields' function, $\gamma\left(\frac{M}{d}\right)^{\frac{2}{3}}$, is really a constant (within very narrow limits of error) for a large number of liquids. At the same time, however, it does not enable us to calculate either the critical temperature of the liquid, such as would be observed; nor does it enable us to estimate the extent of the association of the liquid—if that be the property which causes it to behave differently in this respect from the others.

Applying the results of γ and d, both at the same temperature of observation, t_0, for various liquids, with their gaseous molecular weights, in the equation

$$\gamma\left(\frac{M}{d}\right)^{\frac{2}{3}} = 2.115(t_c - t_0 - 6),*$$

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* Here 2.115 is the average value found from the work of *all* observers on the typical, normal and non-associated liquid, benzene; found by giving t_c its observed value of 288°.5 (critical temperature observed by Young) and employing the experimental values of γ and d for benzene at the various temperatures t_0, using $M = 78$.

he finds that the value of the term, t_c, as calculated for any one liquid, is independent of the temperature of observation, t_0, from which it is found. While in some cases this value of t_c is identical with the observed critical temperature, in others it is not. In the latter case it may be designated as *the fictitious critical temperature*, for as it is the point, 6° below which, according to the equation, the function $\gamma\left(\frac{M}{d}\right)^{\frac{2}{3}}$ attains its zero value, which it should do at the critical temperature, it has a distinct physical significance.

According to Morgan, then, *a liquid is non-associated when the variation with the temperature of* $\gamma\left(\frac{M}{d}\right)^{\frac{2}{3}}$ *is identical with that of the same function for benzene—and this is shown by the finding of identical values of the term* t_c *in the equation,*

$$\gamma\left(\frac{M}{d}\right)^{\frac{2}{3}} = 2.115(t_c - t_0 - 6),$$

at all temperatures of observation, when using the normal benzene constant 2.115, *and the* γ *and* d *of the liquid corresponding to the temperature of observation,* t_0, *with its gaseous molecular weight,* M. Liquids which do not satisfy this definition are of two classes, viz., those which lead to increasing values of t_c with increasing temperatures of observation, and those which lead to decreasing values. In both cases the liquid is abnormal and certainly not non-associated—but even if the liquid is assumed to fail to hold in the equation because of a difference in the molecular weight as a liquid over that as a gas—there is no way of finding the extent of its abnormality or association.

An illustration of this definition from the results of Ramsay and Aston on ethyl propionate is as follows: At $t_0 = 10$, $t_c = 286°.6$; at $t_0 = 46.°2$, $t_c = 286°.1$; and at $t_0 = 78°.2$, $t_c = 286.0$.

These same investigators find for chlorbenzene, at $t_0=45°.6$, $t_c=357°.5$; at $t_0=77°.8$, $t_c=357.7$ and at $t_0=131.3$, $t_c=357°.8$; where Ramsay and Shields find for the same liquid, at $t_0=150°$, $t_c=357°.4$, at $t_0=180°$, $t_c=357°.6$ and for $t_0=200°$, $t_c=357°.9$. In this case the t_c calculated is actually nearly identical with the directly observed value.

Of the 56 pure liquids thus far studied in this way, which by other methods are found to be approximately non-associated (i.e., within limits of error of from 1 to 10%) *all 56 have also been shown to be non-associated by this definition, the t_c values varying in any one case by only a few tenths of one per cent throughout the temperature range studied.*

All ethers, most esters, all hydrocarbons and many other types of liquids have been shown thus to be non-associated—while acids, alcohols, the lower ketones and some other classes have been found to be abnormal. The ketones with molecular weights higher than 100 in general are non-associated—while those with lower values prove to be abnormal.

The molecular weight in the liquid state.—It will be seen from what has been said above, that liquids may be divided into two groups—those which are normal, and lead in certain equations to identical, or nearly identical, constants—and those which, in the same equations, lead to different ones, usually variable with the temperature. This is shown very clearly by the Nernst-Bingham forms of Trouton's law, by the relations of Mills and Crompton, by the relation of Young (Phil. Mag., V, 50, 291, 1900; that the ratio of the actual density at the critical point to the theoretical density, as calculated for a perfect gas, is the same for all substances), by the relation of Ramsay and Shields, and the definition of Morgan and by several others.

In accord with this difference in behavior it is customary to divide liquids into those which are normal, or *non-associated*, and those which are abnormal, or *associated;* the behavior of the latter being assumed, according to the nature of the method used, to be due to the polymerization or association of the liquid, which breaks down with increasing temperature, or to the energy involved in reducing the existing larger molecular weight to that which it possesses as a gas.

CHAPTER IV

THE SOLID STATE*

Remarks.—A solid is a substance which possesses a form of its own., i.e., its shape is not dependent upon that of the vessel in which it is.

Just as we find that a substance contains less energy in the liquid state than it does as a gas, so we find that a solid contains less energy than a liquid, i.e., in going into the liquid state, at the same temperature, it absorbs heat-energy.

Atomic heat. Law of Dulong and Petit.—*The atomic weights of all elements have approximately the same capacity for heat.* A few elements have been found to give different values, but in general for all elements (except boron, silicon, and carbon) we find that at room temperature,

atomic heat = atomic weight × specific heat = 6.34, approximately.

This is the so-called *law of Dulong and Petit*, but it must be remembered that at best it is but a very rough approximation, even for the elements which are not noted as exceptions, the values varying between 5.4 and 6.9. Since the elements change in specific heat differently with the temperature, there could be but one temperature at which such a law could be expected to hold, and we would expect to see it fail at all others. It is true that some attempt to find corresponding temperatures, i.e., equal fractions of the absolute melting-point, have been made—but without much success, for in this case one-half of the elements only seem to lie between 6 and 7 in atomic heat. At the melting-point itself, on the other hand, nearly all the elements give values lying between 9 and 10 (see Lämmel, Ann. der Phys., (4) **23**, 61, 1907).

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* For numerical problems involving the principles discussed here, see Chapter X.

Lewis (J. Am. Chem. Soc., **29**, 1165–1168, 1907) has formulated the following law: *Within the limits of experimental error, the atomic heat at constant volume, at* 20°, *is the same for all solid elements whose atomic weights are greater than that of potassium, and is equal to* 5.9. The relation of this specific heat at constant volume, and that usually experimentally determined at constant pressure, is given by the formula,

$$S_p - S_v = \frac{T\beta^2 v_a}{41.78\alpha},$$

where T is the absolute temperature, β the coefficient of thermal expansion, α the compressibility coefficient, S_p and S_v are the specific heats times the atomic weights, and v_a the atomic volumes, i.e., atomic weight times specific volume. For a formula for calculating the specific heat of solid bodies see also, von Jüptner, Zeit. f. Elektrochem., 1913, 710; 1914, 10 and 105.

At first glance it would seem that the law of Dulong and Petit would enable us to define the molecular weight in the solid state, since the sum of the atomic weights, i.e., the molecular weight, multiplied by the specific heat of the compound should give approximately the same value as is obtained when 6.34 is multiplied by the number of atomic weights in the former. But a moment's thought will show that this relation is only of value in that it insures uniformity in the choice of the atomic weight to be used, and can have nothing to do with fixing the molecular weight of the compound. Thus analysis shows the existence of two chlorides of mercury, the simplest formulas of which are $HgCl$ and $HgCl_2$, but the application of the law of Dulong and Petit does not enable us to state whether the formulas in the solid state are $HgCl$ and $HgCl_2$, or Hg_2Cl_2 and Hg_2Cl_4, any more than the analytical result does.* It is only because the formulas Hg_2Cl_2 and $HgCl_2$ (not Hg_2Cl_4) are found under certain conditions in the gaseous state that they are *assumed* in the solid state.

In all reactions involving solids, then, it is only the actual weight of the reacting substances that is essential, and the very fact that we cannot define molecular weight in the solid state shows its utter lack of chemical or physical significance. If this at any time should be changed, and it appear that the molecular weight does exert an influence experimentally, naturally all our difficulty would disappear, for then a definition could at once be derived from observations of this influence.

Changes in the state of aggregation.—The most important process concerning solids, for our purpose, is their formation from the liquid state, or the formation of the liquid state from them.

If a liquid is cooled very carefully it is possible to reduce its temperature below the solidifying-point and yet have no solid formed. If a crystal of the substance is then thrown in, crystallization takes place immediately, and the temperature rises rapidly to the true solidifying-point. Besides this change in temperature we have also one in volume, since the specific volume in the one state differs from that in the other. And here, just as with boiling liquids, supersaturated states are difficult to avoid, except by the addition of a crystal of the solid phase which is to separate. When that is done the separation immediately takes place, and the perhaps overcooled liquid at once rises to the true freezing-point, i.e., the point at which the solid and liquid phases can exist together in equilibrium, in all proportions.

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* For $HgCl$ we have $(200+35.5)0.052=12.25$, for Hg_2Cl_2 $(400+71)0.052=24.5$; while $2\times6.34=12.68$ and $4\times6.34=25.36$.

When a gas condenses and goes into the liquid state heat is given off. In the same way, heat is also given off when a solid is formed from a liquid, and this is the cause of the rise in the temperature spoken of above. The heat which is liberated by a liquid solidifying (or absorbed by a solid liquefying) is called, for 1 gram of substance, *the latent heat of solidification* (*or fusion*). This heat, referring to 1 mole of substance (i.e., for its molecular weight in grams), is called *the molecular heat of solidification or fusion.*

The effect of pressure upon the solidifying-point may be derived by the consideration of a thermodynamic cycle, just as we did for liquids, p. 94. Starting with 1 gram of the liquid at the temperature T, its absolute freezing-point under the normal atmospheric pressure, p, cool it $\Delta T°$, at which temperature, $T-\Delta T$, it freezes when under the greater external pressure $p+\Delta p$, and allow the solid to form. Here the volume will go from that as a liquid (v_s') to that as a solid (v_s''); and the heat (of solidification) liberated will be $l_{T+\Delta T}$. Since the volume change $(v_s'-v_s'')$ takes place against the pressure $p+\Delta p$, the external work of this process will be $(p+\Delta p)(v_s'-v_s'')$.

Next heat the solid in this state $\Delta T°$, i.e., to $T°$, and allow it to melt under the normal atmospheric pressure p. The heat absorbed (fusion) here will be l_T, while work will be done equal numerically to $p(v_s'-v_s'')$.

The system is now in its original state, i.e., liquid at T under the pressure p. The total work of the cycle of operations through which the system has been carried will be

$$(p+\Delta p)(v_s'-v_s'')-p(v_s'-v_s'')=\Delta p(v_s'-v_s'')$$

and consequently by the second law of thermodynamics (pages 63–66), since l_T is the amount of heat available at T to do work, we shall have

$$\frac{\Delta p(v_s'-v_s'')}{l_T}=\frac{\Delta T}{T},$$

i.e.,

$$\frac{\Delta T}{\Delta p}=\frac{T(v_s'-v_s'')}{l_f},$$

or

$$\frac{\Delta p}{\Delta T}=\frac{l_f}{T(v_s'-v_s'')}.$$

The change in melting-point of a liquid per atmosphere is equal to the product of the absolute temperature, around which the change is to be found, into the excess of specific volume of liquid over solid (in liters), divided by the latent heat of fusion of 1 gram at T° (in liter atmospheres). The *reciprocal* of this expression, then, will simply give *the change in external pressure in atmospheres which is necessary to alter the freezing-point 1° C.*

Here it will be noted that in this form of the Clapeyon-Clausius equation, also, the volume first considered in the term $(v_s'-v_s'')$ is of that state which contains the greater amount of energy (the liquid here), that of the state containing the smaller amount of energy (the solid) being subtracted from it.

This formula is not only of use in case of a change in the state of aggregation, but also for any *reversible* change; for example, that taking place between allotropic forms of the same substance. Thus at 95°.6 C. the rhombic form of sulphur is transformed into the monoclinic form. The reaction is perfectly reversible, an increase of temperature resulting in the production of the monoclinic form, a decrease forming the rhombic. The change in specific volume being 0.014 cc. and the heat of transformation 2.52 cals., both per gram, we have

$$\frac{\Delta T}{\Delta p}=\frac{T\Delta v_s}{l_f}=\frac{(273+95.6)0.000014}{2.52\times 0.041}=0^\circ.05 \text{ per atmos.},$$

where the term l_f is transformed into liter-atmospheres, and v_s into liters, and the result given in degrees per atmosphere; i.e., an increase of pressure of 1 atmosphere increases the transformation temperature by 0°.05, a result which agrees well with the experimental value. On the other hand we find $\frac{\Delta p}{\Delta T}=200$; i.e., to change the transition point 1°, a pressure of 200 atmospheres is necessary.

If the specific volume of the solid is greater than that of the liquid, i.e., if the solid floats upon the liquid (ice in water), the freezing-point, according to the above formula, will be depressed by increased pressure. If, on the other hand, the specific volume of the solid is less than that of the liquid, i.e., if the solid sinks, the solidifying-point will be raised by increased pressure. In the former case the pressure will tend to keep the substance in the liquid form, since that has the smaller volume, and a lower temperature will be necessary to produce the solid; while in the latter case the formation of the solid will be aided by the pressure, and consequently the temperature need not be lowered to such an extent. This is simply another confirmation of the principle of Le Chatelier (page 33), and is always indicated by the sign of $\frac{\Delta p}{\Delta T}\left(\text{or } \frac{\Delta T}{\Delta p}\right)$, for this is negative when the volume as solid is greater than that as liquid, and the negative sign indicates an increase of p (or T), for example, with a decrease of T (or p).

The actual effect of pressure upon the solidifying-point, however, is not large. Thus an increase of pressure up to 8.1 atmospheres depresses the freezing-point of water but 0.059° C.

Here, since we do not have the volume of a gas in the equations, we cannot apply to it $pv_m=RT$, as was done for the case of an evaporating liquid. So far as is known, this equation holds rigidly in this form, just as the simple form of the same equation holds for liquids; the variability of that only being due to the fact that we assume for a simpler form that the gas laws hold without limit.

The above equations give us also *the heat of sublimation*, i.e., of the direct transition from the solid to the gaseous state, if the volumes represent those of solid and gas; or the volume of gas alone may be used by substituting for v the value found from $pv_m = RT$, changing l to Ml or L, i.e., the gram heat to the molecular heat, and v_s to $Mv_s = v_m$.

We have in such a case the two sets of relationships

$$\frac{\Delta p}{\Delta T} = \frac{l_s}{T(v_s' - v_s'')}; \quad \frac{\Delta T}{\Delta p} = \frac{T(v_s' - v_s'')}{l_s}$$

and

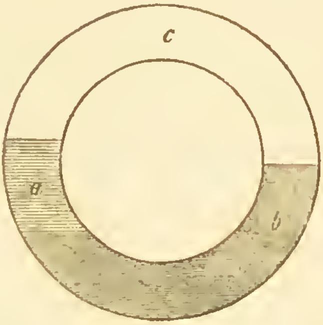
$$\frac{\Delta p}{\Delta T} = \frac{pMl_s}{2T^2}; \quad \frac{\Delta T}{\Delta p} = \frac{2T^2}{pMl_s},$$

when l_s is *the heat of sublimation for 1 gram* of solid going into the gaseous state at an indentical temperature.

Here, just as in the case of the evaporation of a liquid, the first set holds rigidly, for there the work is actually calculated from the change in p and in v; while the second set, since v_s is eliminated by aid of $pv_m = RT$, holds only when that gas law itself holds.

The sublimation-pressure of a solid is to be considered just as the vapor-pressure (i.e., evaporation-pressure) of a liquid. It is noticed that some solids sublime while others melt and evaporate; and the reason for this difference is the fact that when the sublimation-pressure exceeds the pressure of the atmosphere sublimation takes place, and thus keeps the solid from melting. When heated in closed vessels, however, the pressure becomes great enough to prevent continuous sublimation, so that after a small portion sublimes and raises the pressure, the remainder will melt. The principle of this action can also be shown experimentally by heating iodine, which usually sublimes and does not melt, under sulphuric acid, the pressure of which prevents sublimation and allows fusion to take place.

Since at the solidifying- or freezing-point, the solid and liquid states exist in equilibium in all proportions, the vapor-pressure of the solid must be equal to that of the liquid, both at that temperature. That this must be so follows from the following process: Imagine in the annular-shaped vessel, see figure, water at *b*, ice at *a*, and the vapor of the two at *c*: all being at the temperature of 0° C. If the vapor-pressure over the water at *b* is greater than that over the ice at *a*, a distillation from *b* to *a* must take place. By the evaporation at *b* heat will be absorbed, and by the condensation of this vapor to ice at *a*, under the diminished pressure, heat will be liberated. A layer of ice will thus be formed at *b*, while the heat liberated will melt an amount of ice at *a*. We would have, then, an exchange of heat at the same temperature. If this were possible, perpetual motion would be possible; since, however, the latter is impossible, the vapor-pressure of the solid must be the same as that of the liquid, both at the solidifying temperature.



The latent heat of fusion of a solid varies with the temperature just as does that of evaporation, and the expression for it may be derived in a similar manner. The difference in the external work involved in these changes, since no very great change in volume takes place, is so slight that we may consider it as negligible. (1) One gram of solid is allowed to melt at its fusion temperature T, by which the heat absorbed is l_T, and the resulting liquid heated to $T+\Delta T$, which absorbs the heat $s_l\Delta T$. (2) The gram of solid is first heated to $T+\Delta T$, which absorbs the heat $s_s\Delta T$, and then allowed to melt, absorbing the heat $l_{T+\Delta T}$. Since the amount of energy involved in the two processes must be the same, we have

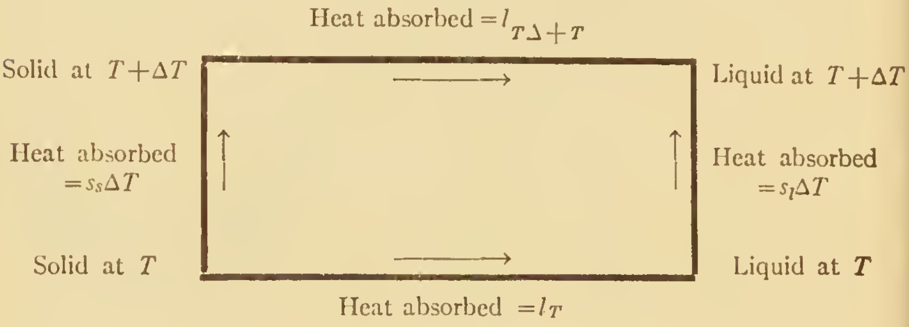
$$l_T+s_l\Delta T=l_{T+\Delta T}+s_s\Delta T$$

and

$$s_l-s_s=\frac{l_{T+\Delta T}-l_T}{\Delta T}=\frac{\Delta l_f}{\Delta T}.$$

The latent heat of fusion increases per degree, around a certain temperature, by an amount equal to the specific heat as a liquid, minus the specific heat as a solid, both at that temperature.

Diagramatically the change of state, together with the energy changes, can be illustrated in the following way, as we have already done in the case of liquids on page 93:


Heat absorbed $= l_{T\Delta+T}$
Solid at $T+\Delta T$
Liquid at $T+\Delta T$
Heat absorbed $= s_s\Delta T$
Heat absorbed $= s_l\Delta T$
Solid at T
Liquid at T
Heat absorbed $= l_T$

By this we see that if the specific heat of the solid is larger than that of the liquid state, the heat of fusion decreases with increasing temperature, for $\frac{\Delta l_f}{\Delta T}$ is negative in sign and consequently the heat increases, as the temperature decreases, and *vice versa*.

In the case of H_2O $s_l=1$, $s_s=0.5$; hence $\frac{\Delta l_f}{\Delta T}=0.5$, i.e., the heat of fusion changes by 0.5 cals. for a change in temperature of 1°. In this case there is a decrease in heat with a decrease of temperature, i.e., the sign of $\frac{\Delta l_f}{\Delta T}$ is positive and temperature and heat increase together.

The latent heat of fusion for water, then, is

$$l_f=80+0.5t.$$

Thus, when freezing at $-4°$, caused by pressure of about 540 atmospheres, l_f for water would be 78 cals. This pressure can be readily calculated, for $\frac{\Delta p}{\Delta T}$ is equal to 135 atmospheres, i.e., $\frac{\Delta T}{\Delta p}$ the change in freezing-point per atmosphere is 0°.0074, so that a 4° depression would require 4×135 atmos. pressure.

From the relation $\Delta T(s_l - s_s) = \Delta l_f$ we can find the change in temperature necessary to reduce the latent heat of fusion to zero, i.e., the temperature at which it passes through the value zero and changes its sign. Thus for water, since $l_f = 80$ at 0°, it would be necessary to lower the temperature of solidification $\Delta T = 160°$ to get zero heat of fusion, i.e., to make Δl_f equal to 80°, for $s_l - s_s = 0.5$.

Tammann (Kristallisieren und Schmelzen, p. 45) gives a list of *absolute* temperatures at which l_f becomes zero, which are derived in this way. Thus we have, for example,

Substance.	Absolute temperature at which $l_f = 0$.
Naphthalene	38
$Na_2S_2O_3 \cdot 5H_2O$	15
Phosphorus	131
$CaCl_2 \cdot 6H_2O$	113
Diphenylamine	130

The variation in the latent heat of *sublimation* with the temperature, can also be calculated by the formula used for the variation of the heat of vaporization, the specific heat of the solid being substituted for that of the liquid (92). We have in this way

$$\frac{\Delta l_s}{\Delta T} = s_p - s_s.$$

The heat of sublimation of a solid changes per degree, around any definite temperature, by an amount equal to the difference between the specific heat of the gas at constant pressure, and that of the solid, both at that temperature. Here we can also represent the changes of state and of energy by a diagram as on page

93, by substituting the solid state, and its properties, for the liquid.

Although in the derivation of the equation on page 121 we assumed that *all* the liquid solidifies at the temperature $T-\Delta T$, this could not happen instantaneously. There is, in fact, a definite relationship between the number of degrees of overcooling and the fraction of liquid which as a result separates at once to form solid. That this must be so is obvious after a moment's thought. Since the freezing-point of a liquid is that point at which solid and liquid can exist together in equilibium in all proportions, it must be the final point attained *after any over-cooling which leaves a portion of the liquid.* According to this, then, only as much solid can separate, after a definite overcooling, as will just bring the system from its overcooled point to its freezing-point; in other words, the weight of solid separated must be such that the heat evolved is just that which is necessary to raise the temperature of the system to the freezing-point. If f is the *fraction* of 1 gram of liquid which is separated as solid, the heat evolved (the heat of solidification per gram), will be l_f, while the heat necessary to raise the system to its freezing-point will be $s_l'\Delta t$. We must have, then,

$$fl_f' = s_l'\Delta t$$

or

$$f = \Delta t\frac{s_l}{l_f'}.$$

The term s_l' here, although referring in reality to the average specific heat of the system liquid-solid between the temperatures t and Δt, may be replaced by the specific heat of the liquid at the freezing-point s_l; and l_f', which really refers to the latent heat at the temperature $t-\Delta t$, may be replaced by the latent heat at $t°$, l_f. This possibility is due to the fact that the change in the specific heat of the system, as well as the variation in the latent heat per degree, depends upon the specific heats in the two states, so that the ratio $\frac{s_l'}{l_f'}$ remains constant no matter what the amount of liquid transformed into the solid state.

If, for example, the fraction f of liquid solidifies, owing to the overcooling Δt, we have as specific heat of the system $(1-f)s_l+fs_s$, and the heat necessary to raise it $\Delta t°$ is $\Delta t[(1-f)s_l+fs_s]$. The heat delivered by the system at $t-\Delta t$, however, according to page 127, is $f[l_f-\Delta t(s_l-s_s)]$ cals., where l_f is the heat of fusion at $t°$, and f is the fraction of the amount of liquid which becomes solid and thus gives out f times l_f cals. The heat delivered by the solidification at $t-\Delta t$ must be just sufficient, then, to raise the temperature $\Delta t°$ to $t°$, hence we have

$$\Delta t[(1-f)s_l+fs_s]=f[l_f-\Delta t(s_l-s_s)],$$

and, by simplification,

$$f=\Delta t\frac{s_l}{l_f}.$$

The fraction of liquid separating as solid, owing to an overcooling, is equal to the number of degrees of overcooling, multiplied by the specific heat of the liquid over the latent heat of fusion, both at the fusion temperature. The specific heat in the liquid state and the latent heat of the liquid, both at the freezing-point may thus be used throughout (in place of the average values, s_l' and l_f') to give the fraction of liquid separated. A specific example will perhaps make this clearer. For water we have $s_l=1$, $s_s=0.5$, while l_f at 0° is 80 cals. When overcooled to $-10°$ C. how much of the liquid is separated as ice?

$$f=\Delta t\frac{s_l}{l_f}=10\tfrac{1}{80}=\tfrac{1}{8},$$

i.e., 125 grams of liquid from each liter will solidify. To check this value we shall calculate the specific heat of the system and see that the amount of heat given out at $-10°$ is just sufficient to raise the temperature to $0°$. The specific heat of the system is $(1-\frac{1}{8})1+\frac{1}{8}\times .5$, i.e., $\frac{7.5}{8}$. The latent heat at $-10°$ is $(80-10\times 0.5)=75$ cals. The ratio, specific heat to latent heat, then, as before, is

$$\frac{\frac{7.5}{8}}{75}=\frac{1}{80}.$$

If a large amount of liquid solute is present, s_l in the above equation must represent the specific heat of the solution. This can be found from the relation,

$$s_{\text{solution}}=\frac{\text{w'g't solute}\times s_{\text{solute}}+\text{w'g't solvent}\times s_{\text{solvent}}}{\text{w'g't solvent}+\text{w'g't solute}}.$$

For strong solutions, we have

$$f=\Delta t\frac{s_{\text{solution}}}{l_f},$$

while for weak solutions,

$$f=\Delta t\frac{s_{\text{solvent}}}{l_f}.$$

We can now consider the quantitative side of a system consisting of liquid, solid and gas in equilibrium, or of a pair of such states, since we have discussed the behavior of each state alone, and its transformation into the others. In the next chapter, from the phase rule point of view, we shall consider briefly the qualitative side of such equilibria, and what conditions their existence.

It is evident, from the law of the conservation of energy, that *at the freezing-point of a liquid, the heat of sublimation of the solid must be equal to its heat of fusion, plus the heat of evaporation of the liquid*; for the same energy difference must exist between the solid and the gas, at the same temperature, whether the solid goes directly into gas, or goes first into liquid and then from that to gas; so long only as the temperature is such that all three states can coexist in equilibrium. We have, then, at the freezing-point of water, for example,

$$l_s = l_f + l_e.$$

Since by definition liquid and solid exist together permanently and in all proportions at the freezing-point under atmospheric pressure, it is plain that at that point the vapor-pressures of solid and liquid must be identical, for otherwise the one would distil to the other through the gaseous space, and would continue to do so until the equilibrium was displaced, and one state of aggregation, only, remained. At all other temperatures, however, the vapor-pressures must be different, under that external pressure, for the values of l_s and l_e are different in the relations,

$$\frac{\Delta p_s}{\Delta T} = \frac{l_s}{T(v_s - v_s'')}; \quad \frac{\Delta p_e}{\Delta T} = \frac{l_c}{T(v_s - v_s')},$$

and it is clear that the change of vapor-pressure for solid is different from that of the overcooled liquid. Here in both cases the specific volumes are negligible against the specific volume, v_s, of the gas, and only the l values are really significant.

The difference in slope of the two curves of change of vapor-pressure with temperature as solid and as liquid can be found, burdened only with the error introduced by the assumption that the simple gas law holds, by aid of the formula found by the substitution of $\frac{v_m}{M}\left(=\frac{RT}{pM}\right)$ for v_s in both the above cases. We have then

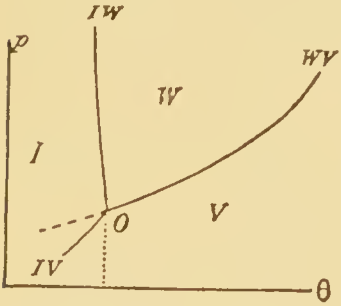
$$\frac{\Delta p_s}{\Delta T}-\frac{\Delta p_e}{\Delta T}=\frac{pM(l_s-l_e)}{2T^2}$$

or, since l_s-l_e at the freezing-point is equal to l_f,

$$\frac{\Delta p_s}{\Delta T}-\frac{\Delta p_e}{\Delta T}=\frac{pMl_f}{2T^2}.$$

i.e., the *difference in slope of the vapor-pressure temperature curves of solid and liquid is equal to the vapor-pressure, times the molecular weight of the substance, times its heat of fusion per gram, divided by twice the square of the absolute freezing-point, at which the vapor-pressure of both is p.* Since both l_f and the term $2(=R)$ are in calories here, the dimensions are fixed by the units selected for the expression of the vapor-pressure p.

The behavior of water in its three states of aggregation is shown by the accompanying figure. Here only at the triple point *O* can the three phases coexist. Any change from that point (0°.00752 at the vapor-pressure of both ice and water, viz., 4.6 mm.) will cause one of the phases to disappear. Thus, cooling the system will cause the liquid to solidify, following the curve *O–IV* (ice-vapor), leaving only solid and vapor in equilibrium—a definite pressure for each temperature. Heating the three-phase system, on the other hand, will cause the ice to melt, leaving liquid and vapor, following the line *O–WV* (water-vapor). And finally raising the pressure of the three-phase system will cause the vapor to condense, leaving water and ice, i.e., following the line *O–IW*.



In case water in contact with vapor is cooled carefully it is possible to pass the point *O*, without the appearance of the solid phase, and we follow the broken line of equilibrium of overcooled water and vapor. In the table below are presented the vapor pressures of ice and of overcooled water for every degree from 0° down to −16° C. It is from these figures that the line *IV* and the broken line were plotted. As will be observed the line *IV* shows a greater change in pressure per degree than the broken line representing the overcooled liquid, as is also shown by the greater change of the pressure of ice in the table.

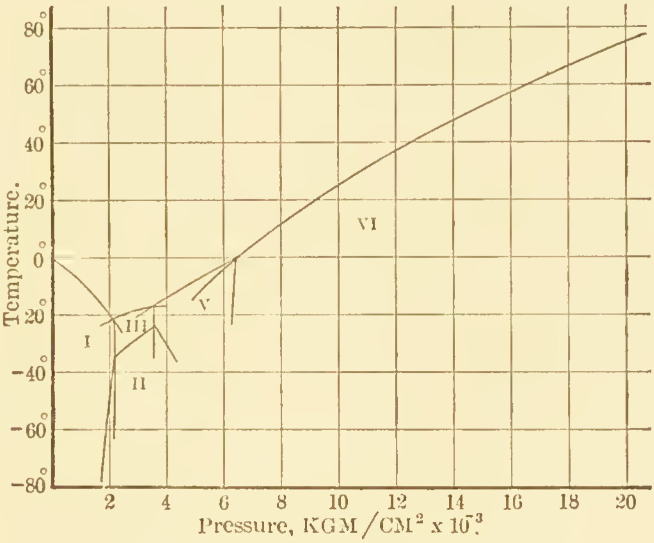
VAPOR PRESSURES

t.	Water. *p* (mm.).	Ice. *p*.
0	4.579	4.579
− 1	4.255	4.215
− 2	3.952	3.879
− 3	3.669	3.566
− 4	3.404	3.277
− 5	3.158	3.009
− 6	2.928	2.762
− 7	2.712	2.533
− 8	2.509	2.322
− 9	2.321	2.127
−10	2.144	1.947
−11	1.979	1.780
−12	1.826	1.627
−13	1.684	1.486
−14	1.551	1.356
−15	1.429	1.237
−16	1.315	1.127

As we found above the freezing-point of water is depressed by increased pressure, although the change is not great—this is shown by the slight slope of the line *IIV* toward the *p* axis. This, however, is not a general behavior of such systems, in fact, but few like it are known. Usually this line will be found to slope away from the p axis at higher pressures, showing an increase in the freezing-point with increased pressure.

In connection with freezing under increased pressure, the question arises as to how ice and water will coexist, with different vapor-pressures, at the freezing-point observed under an increased pressure. In other words what will happen if by greatly increased pressure the freezing-point of water is lowered to −3°, where the vapor pressures are 3.669 for liquid and 3.566 for solid? A moment's thought, however, will show that the system will be forced along the line IW, with the disappearance entirely of the vapor phase, so that there can be no question of a distillation of the one to the other, with the ultimate loss of one of them.

Recently Bridgman (Proc. Am. Acad. Arts and Sciences, 47, 441–558, 1912, and others) has made a complete study, with wonderful experimental skill, of the system—ice and water—under pressures up to 20,000 kilograms per square centimeter, and from −76° to 76° C.; the results of which should be stated, at any rate briefly, in this connection. Instead of finding, as might be gathered from the above, however, that the freezing-point of water (i.e., the point of permanent coexistence of ice and water) could be lowered to *any desired point* simply by increasing the pressure upon the system, he found that the lowest coexistence temperature attainable was a little below −20° C., at a pressure of approximately 2000 kgms. per cm^2. The solid phase here was ice (ice I) as we know it, in every respect except that it was structureless; in other words it had lost its usual crystalline structure under the pressure. The increase of pressure above this point in place of depressing the freezing-point still further, brought with it a sudden decrease in volume and an *increased* coexistence temperature, when the liquid was present; and as the pressure was increased still further, the freezing-point was found to increase, until at a pressure of from 6000 to 6500 kgms. per cm^2., *the freezing-point was once* *again at* 0°. The solid in equilibrium here with the liquid, however, was not the ice I, that we have under 1 atmosphere pressure, but a new modification, ice V, differing from ice I in that *its specific volume* is *smaller* than *water* at the same temperature, while ice I is always *greater* in specific volume than the liquid in equilibrium with it. Increasing the pressure still further, a new modification, ice VI, also with a smaller specific volume, was found to coexist with liquid water up to the highest pressure, viz., 20,000 kgms. per cm.^{2} at 76° C.



Two other modifications of ice are also known, ice III and ice II, the latter only existing when surrounded by solid phases, and never in the presence of liquid water, which disappears below −23° C. An idea of these modifications and the regions of their existence can be obtained from the freezing-point curves above, taken from Bridgman's article.

CHAPTER V

THE PHASE RULE*

Object of the phase rule.—Thus far we have considered the three possible states of aggregation, gases, liquids, and solids, as systems existing alone, and at most have studied the quantitative relations of these as such, and their mutual transformations the one into the other. Although all the *quantitaive* relations possible are thus expressed, there are certain further *qualitative* relations, regulating the equilibrium existing between the states, which have not been touched upon. These relations are summed up in the phase rule, as derived by Willard Gibbs, which is the subject of this chapter.

In order to understand quite clearly the object of this rule, the following systems may be considered: When water is placed in the Torricellian vacuum of a barometer the mercury is depressed, and the extent of the depression increases with the temperature of the water. At any one temperature, however, the pressure is independent of the amount of water present. Water and its vapor, then, can exist permanently side by side, i.e., in equilibrium when, at a given temperature, the pressure has a definite value. If a salt solution be substituted for the water, however, the relation is different. It is true that an increase of temperature still increases the pressure; but the pressure is no longer independent of the volume, for the greater the volume (i.e., the greater the amount of water forming water-vapor), the smaller is the pressure. The presence of solid salt, however, in contact with the solution, causes the pressure to remain constant, irrespective of the actual volume, for this retains the concentration of the solution at its saturated point.

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* For further details on this subject, see Findlay's "The Phase Rule and its Applications," of which I have made free use in this Chapter.

Further, by cooling the water, ice is formed, and so long as this is present with the water the application (or removal) of heat varies neither the temperature nor the vapor-pressure of the system. Thus it is only at one definite pressure and one definite temperature that ice, water and water-vapor can exist together in equilibrium. In the case of a salt solution, on the other hand, we may have ice in contact with the solution at different temperatures and pressures.

The phase rule enables us to decide the necessary conditions for equilibrium in cases of this sort, as well as in all others where an analogous equilibrium is possible.

The phase rule.—Before formulating the law itself it will be necessary to define the terms used by it. A *phase* is a physically distinct, homogeneous and mechanically separable portion of the system; it need not, however, be chemically simple. A gaseous mixture or a solution may form a phase; but a heterogeneous mixture of solids represents as many phases as there are substances present. The dissociation of calcium carbonate thus gives two solid phases, calcium carbonate and calcium oxide, and one gaseous phase, carbon dioxide. It is to be remembered that but one gaseous phase may be present, for all gases are miscible in all proportions. The *components* of a system are those constituents which in concentration can undergo *independent* variation in the different phases. Thus, in the above example, water, not hydrogen and oxygen, is the component; and although calcium carbonate, calcium oxide and carbon dioxide are constituents of the other equilibrium, only two need be considered as components, for the amount of the other is not independent of the amounts of these, but dependent according to the chemical reaction

$$CaCO_3 = CaO + CO_2.$$

Thus taking CaO and CO_2 as the components, the composition of each phase can be easily expressed.

In general, the components are to be chosen from the constituents at equilibrium, and are chosen as the *smallest number* of independently variable constituents necessary to express the composition of each phase participating in the equilibrium, zero and negative quantities of the components being permissible.

The degree of freedom is the number of variable factors, temperature, pressure and concentration of the components which must be arbitrarily fixed in order that the condition of the system may be perfectly defined. Thus a gas has two degrees of freedom, for it is necessary to fix two of the conditions, temperature, pressure or volume, to define it; a liquid and its vapor has but one, for equilibrium at a certain temperature exists only at a certain pressure; while a system of a liquid, its solid and gas, has no degree of freedom, for equilibrium can only exist at a certain temperature and pressure, for otherwise one of the phases will disappear.

Derivation of the phase rule.—Although the following derivation, by Partington (Proc. Chem. Soc., 27, 13, 1911), is not the original one of Gibbs, it may serve to show how such a relation can be deduced without hypothesis and solely by mathematical reasoning.

The assumption is made that it is possible to have a state of equilibrium between several phases at a definite temperature and pressure; this will be characterized by certain definite relations between the compositions of the phases (for example, a solid salt, saturated solution, vapor of the solvent).

Let p and T be total pressure and temperature of the system; n the number of components and r the number of phases.

For each pair of phases there must be some condition satisfied for each component, such that this particular component does not pass from one phase to the other. The r phases may now be arranged in $(r-1)$ pairs, namely, (1, 2), (2, 3), (3, 4) .. . . $[(r-1), r]$, and there will therefore be $(r-1)$ conditions to be satisfied for each component in all the phases, that is, $(r-1)$ equations defining the equilibrium. It is evident that such pairs as (1, 3), (2, 4), etc., need not be considered, since, if phase (1) is in equilibrium with phase (2), and phase (2) with phase (3), then (1) will also be in equilibrium with (3). If this were not the case, we could, by enclosing (1), (2), (3) in a ring-shaped tube, so that there are three surfaces of separation, set up a continuous circulation at a uniform temperature, which is contrary to the second law of the thermodynamics.

For all components there will therefore be $n(r-1)$ equations. The number of variables is made up of

(1) The pressure, p;

(2) The temperature, T;

(3) The number of concentrations $=r(n-1)$, since for each phase we have $(n-1)$ fractions of the total mass for the n components, the last (nth) fraction, being obtained by subtracting the sum of all the others from the total mass, is fixed, and is not an independent variable, therefore, number of variables $=2+r(n+1)$.

The number of variables left undetermined (i.e., changeable), is equal to the number of variables less the number of equations, i.e., is equal to $2+r(n-1)-n(r-1)$ or $2+n-r$.

This number of changeable variables, however, has been called the degrees of freedom of the system, hence, writing it in a different form, we have,

$$F+r=n+2.$$

The number of degrees of freedom of any system is such that when added to the number of phases it must equal the number of components plus 2.

If any component is absent from a particular phase (for example, the vapor phase or the solid phase), there is one variable less, but also, one boundary condition less, for migration of that component cannot occur with respect to the phase considered, and the above equation is therefore still true.

We can summarize the meaning of the equation giving the number of the degrees of freedom of a system, and at the same time translate the phase rule into terms of the graphical representation in a system of coordinates, with respect to pressure and temperature, for example, in the following manner: *In order that a system of n components may exist with no degrees of freedom, i.e., be represented by a point, it is necessary that it be present in* $n+2$ *phases; to have one degree of freedom, and be represented by a line, the n components must be present in* $n+1$ *phases, while for two degrees of freedom and to be represented by a surface, the n components need only be present in n phases.*

Since in the equilibrium of $CaCO_3$ we have two components (CaO and CO_2) and three phases (two solid, CaO and $CaCO_3$, and one gaseous, CO_2), the degree of freedom is $2+2-3=1$. Just as with the univariant system of water and water-vapor (one component in two phases), so this univariant system, or any other, will show a definite pressure for each temperature, between certain limits. The number of degrees of freedom of a system is used in this way as a method of classification of equilibria; and accordingly we have invariant, univariant, bivariant and multivariant systems, the members of each group (no matter what the number of components, so long as F has the same value) behaving identically.

The equilibrium of water in its phases.—The figure on page 132 gives the curves for water when plotted in a system of coordinates of which the abscissas are temperatures and the ordinates are pressures—in other words, the pressure—temperature curves for water, ice and water-vapor. Along the curve WV liquid and gas form a univariant equilibrium.

The curve IV is made up of the values at which gas and solid can exist in univariant equilibrium, i.e., it is the vapor-pressure curve for ice. The curve IW represents the conditions for the coexistence of water and ice. As the freezing-point is but slightly influenced by pressure, this curve forms only a slight angle to the axis of pressures (1 atmos. = depression of 0°.0074).

The point in which the three curves intersect is the *transition-point,* i.e., the triple point in which all three phases can exist in equilibrium. This is at 0°.00752, the pressure being 4.6 mm. of Hg.

If we start with the system containing water and vapor (i.e., down the curve WV) in a closed vessel from which heat can be absorbed, the point of intersection will be reached, part of the water will freeze, and we shall have three phases of one substance, i.e., the transition-point. If the temperature is still decreased either the liquid or the gaseous phase will disappear. Which of these depends upon the ratio of volume. If the volume of vapor is great enough, all the liquid will freeze and the curve IV will be followed. On the other hand, if the volume of liquid is large, all gas will disappear and the curve IW will be produced, for the amount of ice which separates will increase the pressure and thus cause all the gas to condense.

In a system of coordinates, then, as will be recalled from above, *a divariant equilibrium is represented by a surface, i.e., W, V, and I; a univariant equilibrium by a line, as WV, IW, and IV; and an invariant equilibrium by a point, as O;* where the coordinates are pressure and temperature.

A system in an *open* vessel is not usually in true equilibrium, since it tends to lose vapor continually to the surrounding air. Frequently, however, the disturbance of equilibrium due to gain or loss of vapor is slight, and the phase rule may be effectively applied to such open systems—the number of phases r, and the number of degrees of freedom F, each being diminished by 1.

Thus the system $NaCl,H_2O$ in three phases (solid NaCl, solution and vapor) is univariant ($F=1$) in a closed vessel. It is also univariant, however, when exposed to air if we ignore the small readjustments due to loss of vapor, since $F-1=(2-2+2)-1$. And the same holds true of solid, liquid and gaseous water at 0°.

The main point of distinction between the phase rule and the quantitative relations we have discussed before is that the former gives us no information as to the amount of each phase present, but only states that some of it *must be present.*

Solid solutions and compounds.—Assume we dissolve two salts, incapable of reacting, in an amount of water too small to completely dissolve either; ammonium chloride and ammonium nitrate, for example. We would have, then, three independent components and three phases (the two salts and the solution), i.e., a bivariant system and equilibrium can exist under any pressure at every temperature, when it is once established at a given temperature. And the solution saturated with each of the two salts should have a perfectly definite composition, independent of the amounts of the salts and of water.

Using potassium sulphate and ammonium sulphate, however, these relations are not observed; the composition of the solution at equilibrium depends upon the relative amounts of the two salts and water that have been mixed. The addition of one or the other of the two salts causes the solution to become enriched relatively, in amount of the salt added, and poorer in the other salt. This is the behavior of a multivariant system, three components in two phases, i.e., the number of phases can only be two; the two isomorphous salts must form mixed crystals, or a *solid solution* and act together as a single phase.

Suppose ammonia gas is absorbed by a solid. Does the ammonia form with the solid a definite compound, or a solid solution? If a compound is formed we must have three phases: ammonia gas, the solid, and the compound. The system would then be univariant, and for each temperature T there must be a definite dissociation pressure p. If ammonia gas is removed, more of the compound will dissociate and restore the value p. *A fixed dissociation pressure, then, characterizes the presence of a compound;* an example of this is ammonia with the solid metallic chlorides. If a solid solution of gas and solid had been formed, the behavior would have been quite different. The system formed of two phases, ammonia gas and the solid solution, is bivariant; at a single temperature T the system will be in equilibrium for an infinite number of pressures of ammonia gas, i.e., will increase on addition of ammonia and decrease on the removal of ammonia. *The absence of a fixed dissociation pressure characterizes the presence of a solid solution.* An example of this is ammonia gas and solid carbon.

The phase rule and the identification of basic salts.—An exceedingly clever and most important application of the phase rule to inorganic chemistry has been made by Miller and Kenrick.*

In the identification of basic salts we have a problem which up to the present has seemed utterly impossible of accurate solution. By the application by Miller and Kenrick of the phase rule, however, a great field is opened up and there seems to be no reason now why this subject should not be removed entirely from the position of mystery which it has occupied in the past. Naturally analysis alone cannot give much aid in an investigation, for by it it is not possible to tell whether a chemical individual is present or a mixture in varying amounts of two or more chemical individuals.

Applying the phase rule to the formation of basic salts by the action of water on chloride of antimony or on the nitrate of bismuth, the temperature being low and constant and the pressure being atmospheric, we know: (1) that if the system which consists of three components has arrived at equilibrium not more than three phases can coexist. Of these the solution forms one, and the precipitate must be either *one* single homogeneous substance (one phase), or a mixture of two *phases*, for instance, of two basic salts, or of one basic salt with the oxide. (2) That if the observed difference in composition between two precipitates, by the action of different quantities of water on the same salt, is due to their being mixtures of the same pair of basic salts in different proportions, the composition of the mother liquors will be the same in the two cases. (For the solution must be in equilibrium with both phases, whatever their actual amount.) The possible cases can thus be divided into three groups:

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* See Jour. Phys. Chem., 7, 259, 1903, of which I have made very free use.

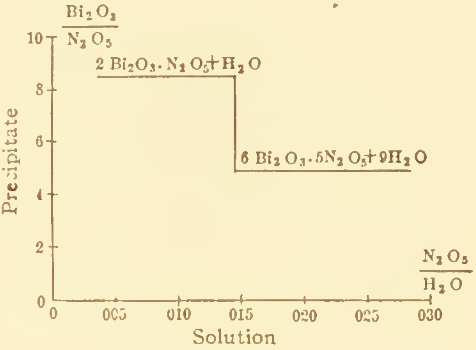
1. The solutions are identical in composition in different experiments, while the composition of the precipitate varies. —The precipitate is a mixture of two phases.

2. The solutions differ in composition, but the precipitates have the same composition.—The precipitate is a single chemical compound.

3. Both solutions and precipitates vary.—The precipitate is a single phase of variable composition, a "solid solution."

If it were possible to represent the compositions of the solution by abscissas, and those of the precipitates by ordinates, the results of a series of experiments could be represented by a curve; perpendicular lines would then correspond to case 1, horizontal lines to case 2, and slanting lines to case 3. In a three-component system this is not possible in general. In many cases, however, a pair or pairs of components may be found whose ratio in the solution or precipitate changes whenever the composition of the solution or precipitate changes, and only then; and since for the interpretation of the results it is only necessary to know whether the composition of solutions and precipitates remains constant or changes from experiment to experiment, it is sufficient to plot these ratios instead of the compositions themselves.

Since in the case of the action of water on nitrate of bismuth the precipitates are all of the general formula $m\mathrm{Bi_2O_3}$, N_2O_5, $n\mathrm{H_2O}$, the compositions of the solutions, also, may be expressed in terms of Bi_2O_3, N_2O_5, and H_2O, which are the components of the system. In the curve below the abscissæ give the ratios between N_2O_5 and H_2O in the solutions, the ordinates those between Bi_2O_3 and N_2O_5 in the precipitates.* The only basic nitrates found are the two noticed in the curve and $Bi_2O_3 \cdot N_2O_5 \cdot 2H_2O$, and all the others which have been supposed to exist were found to be mixtures of these in differing proportions. The vertical line corresponds to mixtures of precipitates, and the horizontal ones to pure chemical individuals.



In the same way Hawley (Jour. Phys. Chem., 10, 654–657, 1906) has proved that white lead is a compound of the composition $PbO_2H_2 \cdot 2PbCO_3$, and not a solid solution. Cox (Jour. Amer. Chem. Soc., 28, 1694–1710, 1906) has applied it to the chromates of mercury, bismuth, and lead; and Bell and Taber (J. Phys. Chem., 12, 171–179, 1908) to copper sulphate, showing that all basic sulphates of copper are simply solid solutions.

It will be seen from this brief sketch that the phase rule itself is not at all difficult to understand, but that its applications may give trouble, owing to the difficulty in choosing the components, and other details. For further, specific, applications to metallurgy and to inorganic chemistry the reader must be referred elsewhere, for here it is only a question of the general principles involved in the law itself.

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* See Allen, Am. Chem. Jour., 25, 307, 1901.

CHAPTER VI

SOLUTIONS *

Definition of a solution.—*A solution is a homogeneous mixture which undergoes a change in composition in producing a new phase* (see p. 137). Thus a solution of sodium chloride, when boiled, gives off the vapor of pure water; and when partly frozen separates pure ice—i.e., in both cases separates a phase different in composition from that of the original system. In case the new phase has the same composition as the remainder, the substance is a *chemical individual* with reference to the formation of that phase; but a change of conditions, a higher tem- and a lower pressure, will often prove it to be really a solution. Thus a 20.2 per-cent solution of hydrochloric acid in water boils, under atmospheric pressure, at 110° and behaves like a chemical individual, i.e., gives off a vapor of the same composition as the liquid it leaves behind; but under a pressure of 2 atmospheres this also proves to be a solution, for the vapor given off by it now contains but 19 per cent of hydrochloric acid. And water vapor, which at lower temperature behaves as a chemical individual, and separates pure water vapor on boiling, and ice (solid water) on freezing, proves to be a solution at a very high temperature, where it breaks down into its constituent gases, hydrogen and oxygen, as will be observed from the experimental figures in the table on page 36. When no possible change we have brought about indicates the presence of a solution or a mixture, the substance is said to be a *chemical element.*

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* For numerical problems involving the principles discussed here, see Chapter X.

The power to form solutions varies with the state of aggregation. Thus for gases it is unconditioned, all gases mixing in all proportions with all others; while for solids, the opposite extreme, it is small, though still present.

Gases in liquids.—A true solution of a gas in a liquid, as we shall consider it here, and to which the laws we are about to discuss can be expected to hold rigidly, is one which does not contain a large amount of the gas, and one in which no chemical reaction has taken place between the constituents. In general, when the law applies, we find experimentally that the gas can be completely expelled from the solution by the application of heat, or by a reduction of the pressure. Wherever this is not possible, then, as in the case of hydrochloric acid gas, for example, where a residue remains which is not removable directly by the above means, we know that the laws cannot be applied.

The solubility, or absorption, of a gas, forming a solution as above defined, can be calculated by the aid of the *law of Henry,* as verified experimentally in a number of cases by Bunsen, viz., *the* WEIGHT *of a gas absorbed or dissolved in a liquid is proportional to the pressure of the gas over the liquid.*

Since pressure and volume (at constant temperature) are inversely proportional, this law may also be expressed as follows: *A given amount of liquid absorbs at any pressure the same, identical, volume of gas, when it is measured at that pressure.* This form, however, it is to be remembered, depends upon the holding of the gas laws, and will fail when the pressure and volume are not inversely proportional, i.e., will only hold when the pressure is such that the product of p and v is constant for the gas under the conditions of the experiment.

By introducing the idea of concentration here (the number of moles of substance, divided by the total volume) instead of the pressure, still another form of this law can be obtained, viz.: *The weight of a gas dissolved by a liquid is such that there is always a constant ratio existing between the concentration of the gas in the liquid, and that in the gaseous space above it.* This ratio is independent of the actual concentrations themselves, and is the same for all concentrations (or pressures), within wide limits; and its magnitude is dependent only upon the natures of the liquid and gas, and upon their temperature.

It is evident, here, from the first of the above forms of Henry's law, that *the weight of any gas absorbed in the unit of volume of a liquid, at any pressure, will be equal to the weight absorbed in that volume at 1 atmosphere pressure, times that pressure*, the temperature as well as the units in which the pressures are expressed, naturally, being identical. And, of course, in any larger or smaller volume of liquid, the weight will be proportionally larger or smaller.

The conventional, fundamental, unit for the quantitative expression of the amount of gas absorbed by a liquid, i.e., the so-called *absorption-coefficient* of a gas, *is the volume of gas (expressed as at 0°) which is absorbed in the unit of volume of the liquid at t° and 1 atmosphere pressure.* Thus at 0°, 1 volume of water absorbs 0.0489 volume of oxygen under the pressure of 1 atmosphere; while at 35°, 1 volume of water absorbs under 1 atmospheric pressure but 0.0244 volume, also expressed as at 0°; so we can say, since the volumes are always given as at 0° and 1 atmosphere pressure, that at 35° but one-half (practically) the *weight* of oxygen is absorbed by a volume of water as would be at 0°. In general, the higher the temperature, the smaller the absorption coefficient of the gas; but the *change per degree* in solubility is dependent both upon the nature of the gas, and upon the solvent.

If instead of a single gas, a mixture of two or more gases (of the type defined above) is absorbed by a liquid, the above laws also hold, in that *each constituent is observed to dissolve,* *from the mixture, to the same extent as it would if it were present alone in a volume equal to the total volume of the mixture; i.e., as if it were alone present in this volume, at a pressure equal to its partial pressure in the mixture.*

An illustration of the principles involved in the calculation of the amounts of gases absorbed in a liquid is given by the following problem: What are the percentages by volume, and by weight, of hydrogen and oxygen dissolved by 500 cc. of water at 0° and 1 atmosphere pressure, from a mixture containing one volume of oxygen to two volumes of hydrogen? The absorption coefficients at 0° of oxygen and hydrogen in water are respectively, 0.0489 and 0.02153.

Here since we have two volumes of hydrogen to one of oxygen, we must always have present in the gaseous state, two *moles* of hydrogen to one of oxygen; and the partial pressures in the mixture at a total pressure of 1 atmosphere, must be $\frac{1}{3}$ atmosphere for oxygen and $\frac{2}{3}$ for hydrogen. Per liter of water, then, we would have absorbed $\frac{1}{3} \times 0.0489 = 0.0163$ liter of oxygen, and $\frac{2}{3} \times 0.02153 = 0.01434$ liters of hydrogen; i.e., 0.00815 and 0.00717 liter dissolve respectively in 500 cc. of water. The percentage *by volume* of the two gases dissolved will thus be 53.2 for oxygen and 46.8 for hydrogen, as compared to the original values in the gaseous state of 33.3 and 66.7. By the absorption, thus, we have enriched the remaining, undissolved gas with respect to hydrogen.

In case the absorption above were made under the same conditions of pressure, etc., *except at 25°*, in place of 0°, where the coefficient of absorption for oxygen and hydrogen are 0.02831 and 0.0178 (both expressed as at 0°), we would find, in a way similar to the above that the volume of the gases absorbed by the 500 cc. of water are 0.00472 for oxygen and 0.000593 for hydrogen, i.e., 44.32 volume per cent for oxygen and 55.68 for hydrogen. The increase of temperature, owing to the unlike change in the coefficients for the two gases, has, as will be seen, caused the mixture going into solution to be enriched in hydrogen over what it was at 0°; and the remaining mixture has been enriched in oxygen at this temperature.

The *weights* of the volumes of the gases absorbed, or the percentages by weight, can be found in an identical way in both the above cases, *for the volumes found are always expressed as at 0° and 1 atmosphere pressure.* We have then in each case a proportion involving simply the volume of a mole under these conditions (22.4), the molecular weight of the gas, and the volume of which the weight is to be found. In this way we find at 0°, 0.01164 gram of oxygen and 0.00128 gram of hydrogen, i.e., 94.79% and 5.21% by weight. At 25° these values are respectively 0.006742, 0.0005295, 92.72% and 7.28%.

Among the striking characteristics of the absorption of a gas in a liquid are the following: There is always less absorption by a solution than by the pure solvent itself and consequently the addition of another, soluble, substance to a liquid already containing a dissolved gas, causes the evolution of a *portion* of the gas. Further, a liquid is very readily supersaturated with a gas, unless points of insoluble substance are present around which gas bubbles may form, on a reduction of the pressure, or on an increase of the temperature. We have already discussed the similar case of the overheating of a liquid, without boiling taking place (see the liquid state), and it is not difficult now to see that in fact it is identical with the above; for then the superheated liquid was simply supersaturated with its own vapor—and we can therefore exceed the boiling temperature by increasing the supersaturation; and in reality only avoid doing so, in general, when points of foreign, insoluble, matter are present.

An experiment which shows in a particularly striking way the possibility of supersaturating a liquid with a gas is the following: Allow carbonic water from a charged syphon bottle to flow into a glass, which has been wiped clean. At first a violent bubbling will be noticed, which, however, will soon cease, leaving the liquid in a state undistinguishable from distilled water. That the liquid is in reality still very greatly supersaturated with the gas, though, can be shown here, even hours later, provided it be protected from the dust floating in the air, by dropping into it a piece of chalk, or a fragment of any other porous substance, when the gas will be evolved so violently from the solid matter, that it will be carried bodily to the surface by the bubbles. Ostwald found in such a case that the CO_2 pressure in the apparently pure water could readily be retained at an internal pressure as high as 2 atmospheres, even though the counter, external, pressure were atmospheric. The original pressure of gas in a syphon bottle is usually about 5 atmospheres.

When a gas of the above defined type is absorbed in a liquid, there is always a change in volume in the latter. As a general rule, the less compressible the gas, the greater is the increase in volume caused by it. This increase in volume of a liquid by the absorption of a gas has been found experimentally to be approximately equal numerically to the constant b in Van der Waals' equation; i.e., the change in volume due to the absorption of an amount of gas, that was 1 liter at 0° and atmospheric pressure, is equal to the value of the correction that would have to be made in the gaseous volume of that weight, under all conditions, according to Van der Waals' equation. In other words, that specific portion of the volume of 1 liter of any gas under these conditions, which is regarded by Van der Waals as being incompressible (by gaseous pressure) in his equation, is also the volume to which that gas is reduced in going into solution.

Further, for any one gas absorbed in various solvents, the volume of the gas in the mixture, i.e., the increase in volume of the solvent, is found to be approximately the same. In other words, this irreducible portion of an original volume of 1 liter is shown to be constant for the gas in various solvents, and thus to be dependent only upon the nature of the gas. This has been proven for air, hydrogen, and carbon dioxide (but certainly would not hold for hydrochloric acid gas, since that falls without our definition with respect to its solution), and is an interesting confirmation of the equations of Budde and Van der Waals.

This minute change in volume due to the solution of a gas in a liquid, i.e., the reduction, in the solution, of the gas to this irreducible minimum, would indicate the presence of enormous internal pressures in the system—of a kind perhaps not to be observed directly in any ordinary way. This pressure would be similar to the *normal pressure* of the liquid mentioned in the discussion of surface-tension. From the view-point of the kinetic theory of gases, it would be attributable to the attraction between the unlike molecules in the solution—and would have to be regarded from the above results as great enough to reduce the volume of the gas to that of the working sphere (incompressible portion) of the gaseous molecules themselves; a pressure, the magnitude of which, can best be realized, perhaps, by examining the tables given under the consideration of the equation of Van der Waals, where in no case was the gaseous pressure applied, great as it was, sufficient to nearly accomplish this.

Before leaving the subject of the solubility of a gas in a liquid, in order to correlate the behavior of such solutions with that of a pure liquid when air is bubbled through it, and to connect it with what we shall find later regarding the distillation of mixed liquids, it will be well for us to see, from our present knowledge, just what would happen to such a system, water containing hydrogen gas, for example, if air were passed through it. We know, here, that with pure water at 0° under such conditions, we are dealing with a *solution of water-vapor at a pressure of 4.6 mm. in liquid water.* In this case, however, we must recognize that the amount of vapor in the solution which can exist *at any one time*, while limited to a pressure of 4.6 mm., is in reality unlimited, for an attempted lowering of the pressure of the vapor of water to a point below 4.6 mm., by blowing air through it, for example, at once causes a new supply to be produced from the liquid, which again restores the vapor-pressure to its original value. In other words, in such a case the gaseous pressure remains constant, even after the removal of some of the gas, which is, of course, quite different from the behavior of a foreign gas dissolved in the liquid.

An original unit volume of air passed through the water, now, will carry off water-vapor with it, so that the pressure of this in the air escaping will be equal to 4.6 mm. In order to retain this volume constant after escape, at what it was originally, then, will require an increased pressure, viz., one equal to 760+4.6, in place of 760. Or, under normal conditions of pressure, that under which the escaping vapor really exists, this unit volume will expand under one atmosphere pressure to a volume equal to $\frac{764.6}{760}$ liters. In this volume, at one atmosphere pressure, the partial pressures will become $\frac{760}{764.6}\times 760$ and $\frac{4.6}{764.6}\times 760$ mm., for air and water-vapor, respectively. The *weight* in grams of water-vapor carried over, then, by the total volume v escaping, as was shown on page 85, can be calculated from the volume of one mole or any gas at $T°$ and p atmospheres, viz., $22.4\frac{760T}{237p}$, together with the molecular weight of the gas, by aid of the proportion $M : 22.4\frac{760T}{273p} :: w : v$; from which the weight of vapor is found to be $w=\frac{Mv\times 273p}{22.4\times 760T}$.

Since p for water here is 4.6 mm., M is 18, T is 273, and $\frac{764.6}{760} = 1.006$ liters (i.e., a total pressure of 764.6 mm. in one liter, corresponds to 760 mm. in 1.006 liters) we find $w = 0.0049$ gram of water vapor carried over by the passage of one liter of air through the liquid.

In case we have hydrogen gas at a pressure of 1 atmosphere, for example, also dissolved in the water, in addition to the water-vapor considered above, each original volume of air passing through the solution, would also increase its pressure in unchanged volume, or increase its volume under the normal atmospheric pressure under which it escapes. The total pressure, here, which is necessary to retain the volume constant, will be equal to the sum of 760 mm. for the air, 760 for the hydrogen gas, and 4.6 mm. for the water-vapor, i.e., 1524.6 mm., or, under 1 atmosphere pressure, the volume would go to $\frac{1524.6}{760} \times 1 = 2.006$ liters. The partial pressures in this volume then would be $\frac{760}{1524.6} \times 760 = 378.86$ mm. each for the air and hydrogen, and $\frac{4.6}{1524.6} \times 760 = 2.28$ mm. for the water-vapor. Substituting these values in the equation found above, we obtain $w_{H_2O} = 0.0049$ and $w_{H_2} = 0.0893$ gram, the total weight of water carried over by one original liter of air, naturally, being the same as in the absence of the hydrogen.

Since air is not a chemical compound, its weight in the mixture can only be obtained from the specific volume, i.e., the volume of 1 gram under these conditions. On page 25, we found for this value, $v_s = 699.8 \frac{760T}{273p}$ cc. so that here we would have

$$\frac{2006 \times 378.86}{699.8 \times 760} = 1.429 \text{ grams.}$$

The weights of the gases escaping from the liquid, per liter of air originally passed through, will of course remain the same as far as concerns the air and water-vapor, so long as liquid water remains present, but the weight of hydrogen will decrease rapidly, according to the volume of liquid containing hydrogen gas (and its original concentration) which is employed; until, finally, all the hydrogen will be removed, and the system left will be pure water with air passing through it—in other words, will be identical with the case discussed on page 85.

As to the mechanism of the process of the removal of a dissolved gas from a liquid, whether it has the same or a different chemical composition, we know that a bubble of gas passing through the liquid, presenting as it does a vacuum with respect to every other gas, will cause the characteristic pressure of this gas to be attained in it, and consequently will remove during its passage enough gas to produce that partial pressure in its volume. Each new bubble will continue to do this, then, so that ultimately all gas will be removed if it be a foreign one, or continuous distillation take place if it is the vapor of the liquid itself. This will enable us to understand more clearly the conditions observed during a distillation of a liquid, where superheating, i.e., supersaturation of a liquid with its own vapor, is prevented by the passage of a current of air through it.

Naturally, in all the above, we are assuming that the mechanical arrangements are such that each bubble *does* become saturated with the gas, but that can now be arranged experimentally.

Liquids in liquids.—We have three possibilities in the case of the solution of one liquid in another.

1. No solubility or a very slight solubility, i.e., the formation of two layers, and no homogeneous mixture.

2. A mutual solubility, but not in all proportions (as water in ether = 3%, and ether in water = 10%).

3. The same relation as with gases, i.e., a solubility in all proportions (as water and ethyl alcohol).

The volume of liquid mixtures is not usually an additive property, for the volume is rarely equal to the sum of those of the constituents. Almost all mixtures possess a volume smaller, but a few larger, than the sum of the partial volumes.

It will be evident here that it is difficult to really distinguish sharply between classes 1 and 2, for the reason that every gas is soluble to a certain extent in every liquid; so that each layer in class 1 would really contain the vapor of the liquid of the other layer, and the behavior would be similar to a liquid in class 2. When this mutual solubility is small the systems, however, can be considered as belonging to class 1.

The miscibility of liquids which do not mix in all proportions, in general, depends upon the temperature, and *usually*, if the temperature be increased, the two layers, or the cloudiness of the system, if it has just been shaken, will disappear, and only one phase remain—the liquids are miscible in all proportions. Thus for phenol and water, up to 68°.4, two layers are always present after the system has been allowed to stand; while above this temperature we have complete miscibility of the two constituents. This temperature of complete miscibility is known as *the critical solution temperature;* and the concentrations of the one substance in the two layers (i.e., at the point where these become identical) is the *critical concentration* of that substance. Above the critical solution temperature, then, only homogeneous solutions exist.

An exception to this behavior with respect to increased temperature, is observed with a system composed of triethylamine and water, where the temperature increase has the opposite effect. In this case it is only *below 18°* that complete miscibility is observed, all temperatures above that producing two layers, i.e., limited, mutual solubility.

And, finally, we find that nicotine and water provide a system which has *two* critical solution temperatures, i.e., at temperatures either below 60° or above 210° we have complete miscibility, while at all temperatures lying between these a limited, mutual, solubility is observed, accompanied naturally by the presence of two layers in the system.

Solids in liquids.—When a soluble solid comes in contact with a liquid it dissolves. *When no more substance is taken up by the liquid at any one temperature, the solid phase being still present, the solution is said to be saturated at that temperature.* There are two general methods of making a saturated solution; but in either it is always to be remembered that *in order that a solution be saturated, the solid substance must be in contact with it.*

I. The substance, in granular form, is brought into the liquid, and the system agitated at a certain temperature until no more is dissolved; or,

II. The solution is made as above, but at a higher temperature than the desired one, to which it is reduced later. The presence of the solid phase in this case insures avoidance of a supersaturated solution, so that solid is deposited from the liquid as the temperature falls, and the solution remains saturated at that temperature.

Both these methods give the same result if properly carried out, although the latter is quicker and is consequently to be preferred.

The importance of the state of the solid from which the solution is made has been pointed out by Hulett (J. Am. Chem. Soc., **27**, 49, 1905). "The explanation of the phenomenon" (of the greater speed of solution and greater solubility of very small particles of solid) "is based on the following considerations: The boundary between a solid and a liquid is the seat of a certain amount of energy due to the surface-energy of the liquid; if this surface is increased by powdering the solid, the total surface-energy is correspondingly increased. Further, it is a generally observed fact that the form of a substance which has the greater free energy is the more soluble, has the greater vapor-pressure, and is the least stable form, e.g., allotropic modifications of substances have different solubilities, and the unstable form is always the more soluble. This phenomenon is hardly analogous to the well-known behavior of liquid drops of different sizes. Small drops in the vicinity of large ones grow small and disappear, while the larger ones grow larger, and the reason is quite clear. It is known that the curved surface of a liquid has a greater vapor-pressure than a plane or less curved surface, therefore, a distillation takes place. The similarity between the vapor-pressure of liquids and the solution-pressure of solids has suggested to some the analogy between the facts just mentioned and the behavior of solid particles of different sizes in contact with the solution. But we cannot assume that the surfaces of the particles of a powder are curved, or, if that is granted, we do not know that a curved surface of a solid or a sharp edge has a greater solution-pressure than a plane surface of the same substance."

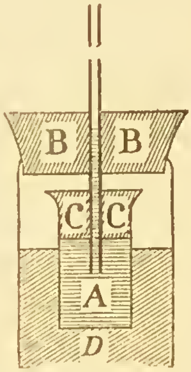
Hulett has found that a solution of gypsum saturated at 25°, containing 2.080 grs. $CaSO_4$ per liter (i.e., 0.01530 mole) will increase its concentration rapidly to a maximum when shaken with *finely powdered* gypsum, and then will decrease to the original value again. In one experiment the content of gypsum reached 2.542 grs. $CaSO_4$ in a liter in a minute. The fine powder used for this purpose was found, after the concentration had reached its original point, to have increased in the size of its grain. The smallest particles thus go into solution, produce the supersaturation and are then deposited upon the others, so that all ultimately increase in size.

For these reasons Hulett advises the preparation of saturated solutions from larger particles, as there is then no danger of supersaturation, and the liquid need not be filtered. In case small particles are used, however, and a supersaturation feared, contact with larger particles or crystals will cause the true equilibrium to be attained from the *supersaturated side.*

It has been observed that crystals dissolve more rapidly in some directions than in others, and it is possible thus to cause a circular disk of gypsum (cut parallel to 010) to become elliptical by the action of dilute hydrochloric acid. Hulett calls attention, however, to the fact that solubility has nothing to do with rate of solubility, *for solubility is measured by the concentration of the solution which is in final and lasting equilibrium with the solid.* He found that the plate of gypsum is equally soluble in all directions, and that a solution saturated with planes cut in one direction is in equilibrium with those cut in other directions. See also in this connection the work of Le Blanc and von Elissafoff (Säch. Gess. d. Wiss., 1913, p. 199) on the solubility of the cube and octahedron faces in the case of rock salt.

It is often possible to cool a saturated solution (which has been separated from its solid phase) to such an extent that it is supersaturated. Some solutions of this sort can be kept indefinitely, provided germs, i.e., particles of the solid phase, be excluded. Such solutions are called *metastable.* On the other hand, there are some solutions in which the solid phase appears even when its germs are excluded. Such solutions are called *labile.* The distinction between these two kinds of solution is not so sharp as one would think, however, for by a sufficient overcooling the metastable solution may pass over into the labile state. In general, the metastable solution is less concentrated than one which is labile. Increase of the concentration causes the metastable state to be transformed into the labile; the concentration at which this occurs being called the *metastable limit.*

Osmotic pressure.—If in a tall jar we place a layer of pure water over a colored solution we observe after a time that the whole liquid is colored. The colored substance has diffused through the liquid until a homogeneous mixture results. This action shows that there must be a certain tendency or pressure which causes the substance to occupy the entire space accessible to it. This pressure causing the substance to diffuse into the solvent is called *the osmotic pressure of that solution.* If a vessel be provided with a partition of such a nature that it allows free passage to the solvent, but not to the solute, and we have water on one side and a solution on the other, the solute will exert a pressure upon it; this is the osmotic pressure of that solution. Semipermeable partitions of this sort had been found by Traube, and perfected by Pfeffer, and by Morse and his co-workers, in such a way that it is now possible to actually measure the different osmotic pressures with great precision by means of a manometer. An apparatus by which the principle of Pfeffer's measurements may be understood is shown in the figure. The cylinder *A* is made of porous clay, and is designed to support the semipermeable film. To produce this the pores of the cylinder are filled with copper sulphate by being placed in a solution of this salt, and the cup is then filled with a 3% solution of potassium ferrocyanide, and allowed to stand for a day in the copper sulphate solution. In this way the pores are filled with a film of copper ferrocyanide, which is permeable to water, but not to a large number of substances. The process of measuring is as follows: The now semipermeable cylinder is washed out and filled with the solution to be measured. The rubber stopper *CC* is next inserted in *A* in such a way that the solution rises a short distance in the tube, i.e., the cylinder is entirely filled with solution without air, and the tube, as it fills with solution, will act as a manometer. The cork *BB* is then fastened in the vessel *D*, which is partly filled with water. Owing to the action of the osmotic pressure the liquid rises slowly in the tube until equilibrium is reached, i.e., until the resistance in the manometer due to the weight of the solution



is just equal to the osmotic pressure. The height of the column of solution, which is heavy enough to prevent more water flowing into the cell, thus represents the osmotic pressure of the solution in A.

There is a definite attraction, then, or an apparent one, between the substance in solution and the solvent, and this is of such a nature that without the partition it would cause the system to become homogeneous. Whether this apparent attraction is actually an attraction between solvent and solute, or whether it is a tendency for the solute to become uniform in concentration in the liquid, owing to forces existing in it, is unknown. As under certain conditions a change in the solvent makes no difference in the osmotic pressure observed (and when it does it can be accounted for quite readily), it would seem that the latter supposition is the more correct one.

However, whether this phenomenon is a pressure or an attraction can have no difference from our standpoint, for what we shall designate as osmotic pressure is an experimentally observed fact which has been given that name. *As such, then, we can define osmotic pressure* (as we shall use the term) *as that pressure which will just prevent pure solvent from going through a semipermeable partition to dilute the solution contained within it.*

The nature of the semipermeable partition seems to have no effect upon the value of the osmotic pressure. That this must be true can be proven by the following process: Imagine A and B (see the figure) to be two unlike semipermeable partitions placed in a cylinder of glass. Assume the cylinder full of solution and lowered in a horizontal position in a vessel of water. If the pressure P_1 is exerted by the partition A, and P_2 (a smaller one) by B, then water will go through A until the internal pressure P_1 is reached. Since B allows only the pressure P_2, however, this

pressure P_1 can never be reached on that side, so that we would have a steady current of water going from A to B, under the finite pressure $P_1 - P_2$. This, however, would be a perpetual motion, which is impossible; hence the partition A must give rise to the same osmotic pressure as the partition B.

Osmotic pressure, then, is independent of the nature of the solvent and the partition, the latter being simply a means of making it visible.

Pfeffer measured, by means of an apparatus of the type of the one described, the osmotic pressures which exist in a large number of solutions and found them in many cases to be very great. A few results for sugar solutions of various concentrations at 15° C. are given in the table below.

OSMOTIC PRESSURES OF SUGAR SOLUTIONS

c.	P.	P/c.	c.	P.	P/c.
1	53.8	53.8	4	208.2	52.1
1	53.2	53.2	6	307.5	51.3
2	101.6	50.8	1	53.5	53.5
2.74	151.8	55.4			

Here c is the percentage composition of the solution, P is the osmotic pressure, in centimeters of mercury, and P/c is the ratio of pressure to concentration.

Considering the difficulties in measuring, and also the probable imperfections in the semipermeable film, the term P/c is to be considered, here, as constant; hence *the osmotic pressure of a solution is proportional to the concentration of the solute.* Further, results at different temperatures showed also that *the osmotic pressure is proportional to the absolute temperature of the solution.* This, however, is only strictly true when the heat of dilution of the solution is zero, i.e., when the solution is dilute.

van't Hoff in 1887 from this much knowledge derived, by the aid of thermodynamics, an analogy between the behavior of gases and substances in solution. Here, however, we shall not go into his reasoning, but shall see how the same results may be obtained in a more simple manner.

As apparent from Pfeffer's results, the term P/c remains constant for any one solution, where P is the osmotic pressure and c the concentration. $1/c$ (c being given in grams per 100) however, is equal to v_s, the volume containing 1 gram; we have then

$$P/c = Pv_s.$$

Since now the osmotic pressure is also proportional to the absolute temperature, as is, therefore, the term P/c, we have

$$Pv_s = \text{constant} \times T.$$

This equation is so much like the one for gases (1) that it immediately suggests that there is some kind of a connection between the behavior of gases and that of substances dissolved in a solvent. If we find the value of this "constant," and compare it with the *gas constant*, it will be possible to find then, just what this connection is. Since the molecular gas constant is a more general concept, we shall make this comparison through it. A solution of 1 gram of sugar in 100 cc. of solution sugar at 0° is held in equilibrium by a column of mercury 49.3 cms. high, and thus gives an osmotic pressure equal to

$$49.3 \times 13.59 = 670 \text{ grams per sq.cm.}$$

Since the molecular weight of sugar ($C_{12}H_{22}O_{11}$) is 342, the volume in which 1 mole must be dissolved, to give this strength of solution, is 34,200 cc. We have then

$$\text{constant} = \frac{P_0 v_{m,0}}{T} = \frac{670 \times 34200}{273} = 84000 \text{ gr.-cms.},$$

while the molecular gas constant is

$$R = 84780 \text{ gr.-cms.}$$

The constant is the same, then (within the experimental error), for the gaseous state and the state of a substance in solution; consequently for each state, considering 1 mole, we have

$$Pv_m = RT.$$

van't Hoff summed up these results in the following form: *The osmotic pressure of a substance in solution is the same pressure which that substance would exert were it in gaseous form at the same temperature and occupying the same volume.*

Since 1 mole of gas at 0° and 76 cms. would occupy the volume of 22.4 liters, at the volume of 1 liter it will have the pressure of 22.4 atmospheres (Boyle's law). This pressure, 22.4 atmospheres, is then the osmotic pressure, *according to van't Hoff's law,* which is exerted by 1 mole of solute in 1 liter of solution at 0°, i.e., by a *molar* solution. From this osmotic pressure, 22.4 atmospheres, it is very easy to find that for any other concentration, given in terms *molar.* Thus a *m*/10 solution *of any substance, in any solvent,* should give an osmotic pressure of 2.24 atmospheres at 0° C.

Morse and Frazer (Am. Chem. J., 1905 to 1913), in an apparatus similar to that of Pfeffer, but greatly refined, have measured the osmotic pressures of sugar and glucose solutions up to 25 atmospheres. Their results for strong solutions of sugar at 20° show that van't Hoff's law holds, *provided the volume of pure solvent is substituted in the law for that of the solution.* In place of the above law

$$P = \frac{RT}{v_m},$$

where v_m is the volume of the solution which contains 1 mole, they find that

$$p = \frac{RT}{v_m'},$$

where v_m' is *the volume of the pure solvent which contains* 1 *mole*, corresponds more closely with their experimental results.

Morse and Frazer sum up their results as follows: "*When we dissolved a gram-molecular weight of cane-sugar (342.22 grams) in 1000 grams of water, i.e., in that mass of solvent which has the unit volume, 1 liter, at the temperature of maximum density —we found its osmotic pressure, at about 20°, in quite close accord with the pressure which a gram-molecular weight of hydrogen would exert, at the same temperature, if its volume were reduced to 1 liter, i.e., to that volume which the unit mass of solvent has at the temperature of greatest density.*"

For cane-sugar, then, and presumably for all other substances, we can express the law as follows: *A substance in solution* "*exerts an osmotic pressure equal to that which it would exert if it were gasified at the same temperature, and the volume of the gas were reduced to the volume occupied by the solvent in the pure state.*" Or, in other words, "*the substance exerts an osmotic pressure throughout the larger volume of the solution equal to that which as a gas it would exert if confined to the smaller volume of the pure solvent.*" This correction might be considered as equivalent to that introduced in the gas laws by the Van der Waals constant, b, i.e., the use of the smaller volume $v-b$, in place of the usual v. For sugar solutions, the molecular weight of this substance being so large, the correction thus introduced would be considerable.

This law of van't Hoff's, as modified by Morse and his co-workers, enables us now to define the molecular weight of a dissolved substance, and the definition naturally reminds one of that definition for substances in the gaseous state. *The molecular weight of a substance in solution is the weight in grams which in the volume of 22.4 liters of solvent will give an osmotic pressure of 1 atmosphere at 0° C., or a corresponding value at another temperature, or in another volume.*

If the osmotic pressure of a solution is known, it is then possible to find from it the molecular weight of the dissolved substance. A solution of 2 grams of sugar in 100 grams of water, gives, at 0° C., an osmotic pressure equal to 101.6 cms. If this solution contained 1 mole in 1000 grams of water it would give a pressure equal to $22.4 \times 76 = 1702.4$ cms. The solution we have used contains 20 grams to the liter; hence $20 : M :: 101.6 : 1702.4$, i.e., $M = 335$.

Results for sugar and glucose obtained by Morse and his co-workers are summarized in the following tables, and will serve to show the agreement between the determined values

OSMOTIC PRESSURES OF CANE-SUGAR

Weight Normal Concentration.	Temperature of Solution.	Observed Osmotic Pressure. Atmospheres.	Theoretical Gas Pressure at same Temperature. Atmospheres.	Difference between Osmotic and Gas Pressure.	Molecular Weight Calculated from Osmotic Pressure.	Mean Molecular Weight for Each Concentration.
0.1	24°.06	2.51	2.42	+0.09	327.85	325.21
0.1	24°.23	2.55	2.43	+0.12	322.56	
0.2	20°.90	4.72	4.79	−0.07	344.96	341.87
0.2	21°.38	4.78	4.80	−0.02	344.90	
0.2	21°.77	4.81	4.81	0.00	339.74	
0.3	21°.67	7.24	7.21	+0.03	338.37	338.29
0.3	19°.88	7.20	7.16	+0.04	338.20	
0.4	21°.63	9.64	9.61	+0.03	338.73	338.12
0.4	22°.15	9.69	9.63	+0.06	337.50	
0.5	22°.62	12.06	12.06	0.00	339.59	337.89
0.5	23°.70	12.23	12.10	+0.13	336.19	
0.6	24°.38	14.74	14.55	+0.19	335.32	335.24
0.6	24°.24	14.70	14.55	+0.15	336.07	
0.6	24°.10	14.77	14.54	+0.23	334.32	
0.7	23°.64	16.95	16.94	+0.01	339.39	339.45
0.7	23°.90	16.96	16.93	+0.03	339.50	
0.8	23°.60	19.30	19.35	−0.05	340.48	339.78
0.8	23°.69	19.39	19.36	+0.03	339.08	
0.9	24°.79	21.82	21.86	−0.04	340.19	339.51
0.9	24°.76	21.91	21.86	+0.05	338.82	
1.0	23°.56	24.42	24.19	+0.23	336.39	339.56
1.0	24°.58	23.98	24.28	−0.30	342.72	

H=1

Final mean of mol. weight, 337.49
Theoretical mol. weight, 339.60

OSMOTIC PRESSURES OF GLUCOSE

Weight Normal Concentration.	Temperature of Solution.	Observed Osmotic Pressure. Atmospheres.	Theoretical Gas Pressure at Same Temperature. Atmospheres.	Difference between Osmotic and Gas Pressure.	Molecular Weight Calculated from Osmotic Pressure.	Mean Molecular Weight for Each Concentration.
0.1	24°.10	2.39	2.42	−0.03	181.40	180.62
0.1	25°.10	2.42	2.43	−0.01	179.83	
0.2	24°.10	4.76	4.85	−0.09	181.77	181.94
0.2	24°.93	4.77	4.86	−0.09	182.10	
0.3	22°.20	7.12	7.22	−0.10	181.38	181.06
0.3	23°.48	7.17	7.25	−0.08	180.73	
0.4	26°.90	9.70	9.78	−0.08	180.21	180.62
0.4	26°.60	9.65	9.77	−0.12	181.02	
0.5	21°.86	12.07	12.03	+0.04	178.12	179.35
0.5	24°.17	12.00	12.12	−0.12	180.57	
0.6	22°.57	14.56	14.46	+0.10	177.62	179.62
0.6	22°.40	14.32	14.40	−0.08	180.42	
0.6	22°.30	14.29	14.45	−0.16	180.83	
0.7	22°.26	16.82	16.85	−0.03	179.18	179.63
0.7	25°.43	16.96	17.04	−0.08	179.55	
0.7	22°.70	16.75	16.88	−0.13	180.16	
0.8	23°.00	19.27	19.31	−0.04	179.16	179.76
0.8	23°.28	19.16	19.33	−0.17	180.39	
0.8	23°.64	19.25	19.35	−0.10	179.73	
0.9	23°.80	21.64	21.80	−0.16	179.87	179.9
0.9	22°.58	21.49	21.70	−0.21	180.49	
0.9	23°.10	21.63	21.74	−0.11	179.60	
1.0	22°.20	24.12	24.08	+0.04	178.46	179.04
1.0	22°.60	24.00	24.11	−0.11	179.60	
1.0	22°.10	24.03	24.07	−0.04	179.07	

H = 1. Mol. wt. glucose = 178.74. Mean mol. wt., 180.08.

and those calculated in this way. It is to be remembered here that the dilute solutions are more affected by the experimental and unavoidable error than the others, so that the apparently abnormal figures for the 0.1 molar solution may be disregarded. The molecular weight here is calculated from the more general form of the above proportion, viz.,

$$M : 22.265\frac{273+t}{273} :: w : P,$$

where 22.265 is the volume of 2 grams (not 2.02) of hydrogen at Baltimore, M is the molecular weight of substance dissolved in 1 liter of water, and P is the observed osmotic pressure at the temperature t, when w grams of the substance are dissolved in 1 liter of water.

In one of the tables below are given the osmotic pressures of ten strengths of sugar solutions at a number of temperatures, and in the other are the more convenient forms of ratios of experimental osmotic pressures to the gas pressures, such as would be calculated, considering the substance to exist as a gas, in a volume equal to that of the pure solvent, at the same temperature; in other words from $pv_m = RT$.

WEIGHT-NORMAL CONCENTRATION OF CANE-SUGAR

Temp.	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	1.0
	Mean Osmotic Pressure in Atmospheres									
0°	(2.462)	4.722	7.085	9.442	11.895	14.381	16.886	19.476	22.118	24.825
5°	2.452	4.818	7.198	9.608	12.100	14.605	17.206	19.822	22.478	25.283
10°	2.498	4.893	7.334	9.790	12.297	14.855	17.503	20.161	22.884	25.693
15°	2.541	4.985	7.476	9.949	12.549	15.144	17.815	20.535	23.305	26.189
20°	2.590	5.064	7.605	10.137	12.748	15.388	18.128	20.905	23.717	26.638
25°	2.634	5.148	7.729	10.296	12.943	15.624	18.434	21.252	24.126	27.053
30°	2.474	5.044	7.647	10.295	12.978	15.713	18.499	21.375	24.226	27.223
40°	2.560	5.163	7.844	10.590	13.355	16.146	18.932	21.803	24.735	27.701
50°	2.635	5.278	7.974	10.724	13.504	16.319	19.202	22.116	25.123	28.213
60°	2.717	5.437	8.140	10.866	13.666	16.535	19.404	22.327	25.266	28.367
70°	....	......	.....	......	13.991	16.820	19.568	22.567	25.562	28.624
80°	....	......	.....	......	......	......	......	23.062	25.919	28.000

From the table of ratios below, it will be observed, that the deviations of the calculated from the observed pressures of Morse and his co-workers are found in all cases below 25°, and that are greater in the case of concentrated solutions than in dilute. At higher temperatures, however, the deviations gradually disappear, so that at 80° they no longer exist even for the most concentrated solutions, and Boyle's law holds.

For any given concentration for the temperatures below 25°, the ratio of osmotic to gas pressure is constant, which indicates that the law of Charles (or Gay-Lussac) holds also for osmotic pressure, i.e., the osmotic pressure changes with the temperature just as gaseous pressure would. At temperatures above 25°, however, this law no longer holds, the ratio of osmotic to gas pressure varying with the concentration.

WEIGHT-NORMAL CONCENTRATION OF CANE-SUGAR

Temp.	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	1.0
	Ratio of Osmotic to Gas Pressure									
0°	(1.106)	1.061	1.061	1.060	1.069	1.077	1.083	1.093	1.104	1.115
5°	1.082	1.063	1.058	1.059	1.067	1.074	1.084	1.093	1.102	1.115
10°	1.082	1.060	1.059	1.060	1.066	1.073	1.083	1.092	1.102	1.113
15°	1.082	1.061	1.061	1.059	1.068	1.073	1.083	1.093	1.102	1.115
20°	1.084	1.062	1.060	1.060	1.067	1.073	1.084	1.093	1.103	1.115
25°	1.084	1.059	1.060	1.059	1.065	1.071	1.083	1.093	1.102	1.113
	(1.083)	(1.061)	(1.060)	(1.060)	(1.067)	(1.074)	(1.083)	(1.093)	(1.103)	(1.114)
30°	1.000	1.020	1.031	1.040	1.050	1.060	1.069	1.081	1.089	1.101
40°	1.003	1.011	1.024	1.038	1.046	1.054	1.059	1.067	1.076	1.085
50°	1.000	1.002	1.009	1.017	1.025	1.032	1.041	1.049	1.059	1.071
60°	1.000	1.001	0.999	1.000	1.006	1.015	1.020	1.027	1.033	1.044
70°	.....	.....	.....	.....	1.000	1.002	0.999	1.008	1.015	1.023
80°	.....	.....	.....	.....	.....	.....	.....	1.001	1.000	1.000

The tables thus show that neither the law of Boyle nor the law of Charles holds rigidly over this range of concentrations and temperatures; and this fact accentuates the simplifying assumptions made by van't Hoff in his derivation of the law.

One thing of especial importance to bear in mind, in correlating the laws of osmotic pressure with the others, which allow a determination of the molecular weight in solution, is that it is dependent upon the number of *moles* dissolved in a *volume* of solvent, and the temperature.

Lewis (Jour. Am. Chem. Soc., 30, 668–683, 1908) in a theoretical paper has called attention to this fact that the modified form of van't Hoff's equation, presented by Morse and Frazer, as epitomizing their results, is not satisfactory at higher concentrations, and advocates the equation (see also later),

$$P-\tfrac{1}{2}\alpha P^2=-\frac{RT}{v_m}\log_e x,$$

where α is the compressibility of the solvent, v_m its molecular volume (volume which contains 1 mole), and x is the molar fraction of the solvent, i.e., moles of solvent divided by moles of solute plus moles of solvent.*

Lewis also calls attention to the fact that the osmotic pressure at one temperature may be found from that at another if the heat of dilution of the solution is known.

Measurements of the osmotic pressures of strong solutions of sugar, galactose, mannitol, and dextrose, have also been made by Berkeley and Hartley (Proc. Roy. Soc., **73**, 433, 1904; Trans. Roy. Soc., **206**, 481, 1906).

It is not only water solutions that have been measured, however, for Raoult (Zeit. f. phys. Chem., **27**, 737, 1895) has found that vulcanite allows passage to ether but not to methyl alcohol. Thus with ether on one side, and an equal volume mixture of ether and methyl alcohol on the other, he observed an osmotic pressure of 50 atmospheres at 13° C., when, as the manometer was then fractured, no higher pressures obtained could be read. In this case the pressure, just as with water solutions, was exerted in the solution, i.e., the pure solvent goes toward the solution, and a pressure is necessary to prevent it.

There is one characteristic of osmotic phenomena which must be mentioned. It is the slow rise of the pressure up to its maximum value. Thus with a half-molar sugar solution Morse and Frazer found 95 hours necessary for the establishment of the final equilibrium. This, naturally, is to be attributed to the resistance of the cell to diffusion.

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* 1 mole in a liter of water (i.e., $\frac{1000}{18}=55.5$ moles) gives a value of x equal to $\frac{55.5}{55.5+1}=0{,}0982+$.

The effect of osmotic pressure can also be observed without the use of the elaborate manometric method above mentioned.

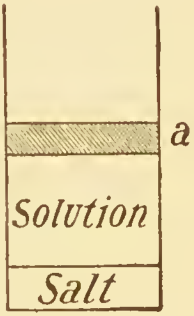
A simple and quick method for this purpose is given by Tammann. If in a moderately strong solution of copper sulphate, we place a drop of a strong solution of potassium ferrocyanide it is immediately surrounded by a semipermeable film of copper ferrocyanide. Since the ferrocyanide solution is more concentrated than that of the copper sulphate, water goes through the film, from the copper salt to the ferrocyanide, and *dark* streaks are observed to sink from the bubble. These streaks are of stronger copper-sulphate solution, which is formed from the other by the loss of water, and sink on account of their increased specific gravity. If the ferrocyanide solution is weak and another salt, or more ferrocyanide, is added to it until no streaks are observed to sink from a bubble, then there must be an equal number of moles per liter in both of the two solutione, i.e., in the copper solution and the ferrocyanide plus salt. If the ferrocyanide solution is weaker than the one of copper sulphate (in moles per liter), water will go out of the bubble, which will decrease in size, and *tight* streaks will appear in the copper solution.

In this experiment the tendency for the solutions to become of the same molar concentration is particularly striking, and water is always observed to go from the more dilute to the more concentrated, the concentrations being expressed in moles per liter.

Consider a cylinder, as shown in the figure, filled with a solution, and provided with a semipermeable piston *a*. If by a certain weight this piston is lowered, water will go through it, and we shall have separated an amount of solvent from the solution. If the amount of water separated previously contained 1 mole of solute, and the total volume is very large, the osmotic work is given by the equation

$$Pv_m = RT,$$

where v_m is the decrease in the volume occupied by the solute under the constant osmotic pressure P. It is possible thus to determine the molecular weight of any substance in solution by calculating the work necessary for the separation from it of a certain amount of the solvent. For each amount of solvent which has previously contained one mole of solute the work is (just as for gases) $2T$ cals., so that the number of moles in the definite amount of solvent removed may be calculated from the work, and from this the molecular weight of the solute can be found. *The molecular weight of a substance in solution by this method would be the weight which has been dissolved in that volume of solvent requiring the work 2T cals. to remove reversibly from the main portion of the solution.* It will be noted here that the concentration of the solution need not be considered, for while the volume, if it were weak, would be large, and if it were strong, would be small, the product of pressure and volume would be constant. For an excellent monograph on osmotic pressure, see Findlay, Osmotic Pressure, London, 1913.



Solution pressure.—The pressure with which a solid goes into solution is called its *solution pressure*. This term, naturally, is expressive of the fact that when the substance has dissolved it exerts osmotic pressure. Since the osmotic pressure increases with the amount of substance dissolved, the solution pressure of a substance can be no greater than its osmotic pressure in a saturated solution, for that pressure is, by definition, sufficient to prevent the substance from dissolving further. A substance is less soluble in its own solution than in pure water, and it seems that it is the osmotic pressure which is due to that substance itself which effects its solubility principally, except perhaps in the case of a very soluble substance; at any rate, no general law is known which governs the solubility of a substance in solutions of other substance, i.e., when the solution pressure is counteracted by an osmotic pressure due to another substance. The behavior of a substance dissolving, then, is very similar to a substance going into the gaseous state, and we may consider that we have a solution pressure of a solid, corresponding to the vapor-pressure of a liquid.

The vapor-pressure of solutions.—In considering the subject of the vapor-pressure of solutions, we shall start with those systems made up of two liquids, then go to the case of a solid dissolved in a liquid, and, finally, when we are properly equipped with the necessary laws, will return again to the subject of the vapor-pressures of mixtures of liquids which mix in all proportions.

Recalling the subdivision we made in discussing the solubility of liquids in liquids (page 156), let us now consider these mixtures from the point of view of their distillation. We shall discuss first (1) cases where two completely immiscible liquids are present; next (2) those which have a mutual solubility; and finally (3) those for which the mixture is homogeneous.

1. A liquid which consists of two immiscible constituents, present in two layers, has a vapor-pressure equal to the sum of the vapor-pressures of the constituents. The boiling-point of such a system, then, which is that temperature at which the total vapor-pressure becomes equal to the pressure of the atmosphere, must lie still lower than the boiling-point of the lower boiling constituent. This is difficult to observe experi-

mentally by direct heating, owing to the bumping. If, however, the vapor of another boiling liquid is passed through the mixture, the whole is heated evenly and to the same degree, and the mixture is observed to actually boil and distill at a point below the temperature at which either constituent alone will. An example of vapor-pressure as an additive property in such a system is given by a mixture of water and carbon disulphide. At 26°.87 the vapor-pressure of water is 26.3 mm., and that of carbon disulphide is 388.7, consequently the total vapor-pressure of the mixture, according to this law, should be 415.0, while experiment shows 412.3 mm.

The vapor-pressure of such a mixture, since each liquid is present in the pure state, and unaffected by the other, must be equal to the sum of the partial pressures of the constituents at that temperature; just as it would be over a system, which, while containing the two liquids in separate vessels, would allow the vapors to form in a common air space.

In such a case for permanent equilibrium, whether the liquids are together in two layers or separated, enough of each liquid must be transformed into the gaseous state to give, at that temperature, in the total gaseous volume, the characteristic partial pressure it would give were it alone. Designating the two liquids by the subnumerals, 1 and 2, we would have, then, for the total vapor-pressure over the system $p=p_1+p_2$. The total number of moles, present in the total volume of gas, would then be N_1+N_2; and the *molar fractions* (x) *of the constituents in the gaseous phase* would be $x_1=\frac{N_1}{N_1+N_2}$ and $x_2=\frac{N_2}{N_1+N_2}$. Since the partial pressures will be proportional to the number of moles, the *fractional pressures*, $\frac{p_1}{p_1+p_2}$, and $\frac{p_2}{p_1+p_2}$, must also be equal to x_1 and x_2, respectively.

We found on page 154 that the weight of a volume of v liters of any gas, under the conditions T° and p *mm.* pressure, is

$$w=\frac{Mv\times 273p}{22.4\times 760T}\text{ grams.}$$

Applying the specific values of the two immiscible liquids existing in a system to this equation, since the temperature, T, and the volume of the air space, v, and the terms 273, 22.4, and 760 would necessarily be identical for both, we find,

$$w_1 : w_2 :: M_1p_1 : M_2p_2.$$

The weights of two immiscible liquids distilling, at any one temperature, into any gaseous volume, are proportional to the products of their vapor-pressures in the pure state, at that temperature, into their molecular weights in the gaseous state; or, for every hundred grams of distillate, we would have

$$w_1 : 100-w_1 :: M_1p_1 : M_2p_2,$$

where w_1 would be the percentage by weight of one constituent, and $100-w_1$ would be that of the other.

Naturally, here, since the density of a gas, *based upon the density of hydrogen as a unit,* is equal to one-half the molecular weight as a gas, we can substitute for the above M values the terms $2\delta_H$. It would also be possible, of course, to substitute the density in terms of the density of water at 4° (the weight of 1 cc. in grams) for the M's, but in that case the *absolute* values of each would depend upon the temperature, although their ratio would remain the same. This accentuates the value of δ_H as compared to d, in such calculations, for so long as the molecular weight remains unchanged, δ_H will remain constant, since it is in terms of the density of hydrogen under the same conditions, and the two gases must vary together, leaving the term δ_{II} constant. The actual weight of 1 cc. of the gas, d, on the other hand, changes both with temperature and pressure.

An illustration of the above law of distillation from immiscible systems, which seems to hold rigidly under all conditions, is the following. A mixture of naphthalene ($M_1 = 128$) and water ($M_2 = 18$) is found at 98°.2 to have a vapor-pressure of 733 mm. At this temperature, the vapor-pressure of pure water is 712.4, and that of naphthalene is 20.6 mm., hence the weights per hundred grams of distillate, under this reduced pressure, would be

$$w_1 : 100 - w_1 :: 20.6 \times 128 : 712.4 \times 18$$

or $w_1 = 17.05$, $w_2 (= 100 - w_1) = 82.95$ grams.

The result here is especially striking, for it shows that if one constituent has a large molecular weight, compared with the other, it will distill in considerable amounts, even though its vapor-pressure at that temperature be small.

Naturally, in all such systems, neither the absolute nor the relative amounts of the liquids are to be considered at all; for so long as each is present the above law will hold. The same laws would also hold for a system containing more than two layers, i.e., more than two immiscible liquids, the weight of each distilling being proportional to its vapor-pressure times its molecular weight as a gas.

This law is the basis of our distillations by aid of live steam. It will make no difference, naturally, whether steam is passed through the second liquid constituent alone, or through a mixture of that and water, or whether simply a current of heated air is passed through the mixture of the two. In all cases the result, as far as the percentages distilled, are concerned, will be the same; and the relative amounts of the two liquids distilled will depend in all cases only upon their molecular weights in the gaseous state, and upon their vapor pressures when pure.

The passage of heated air or steam through the mixture, in addition to the above effect, which could be obtained without it, by distilling the mixture of two liquids in some other way, has the decided advantage of heating the system uniformly, thus preventing "bumping"; and, further, insures, as was shown in the consideration of the solubility of gases, that no supersaturation of the gas or vapor can exist in the liquid, i.e., that no superheating (without the giving off of the proper amount of vapor) can occur.

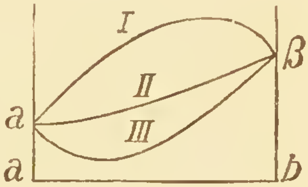
2. In the case of a mixture of *partially* miscible liquids, i.e., where each is mutually soluble in the other, we have also a constant boiling-point and a constant distillate so long as two layers remain. The boiling-point here may be higher, equal to, or, as for class 1, lower than that of the lower boiling liquid. It cannot, however, be higher than that of the higher boiling constituent. With regard to the vapor-pressures of the two layers formed when the two constituents are to a slight degree mutually soluble, Konowalow has shown that *the liquid B when saturated with A has the same vapor-pressure as the liquid A when saturated with B, both being at the same temperature.* It is apparent, then, if this be true, that it makes no difference which layer is above in a distillation, since both have the same vapor-pressure, and consequently both give off vapor of the same composition at the same temperature. As an example of the above behavior of such systems, Konowalow found that at 19°.8 ether saturated with water exhibits a vapor-pressure of 432.2, while water saturated with ether at that temperature has a vapor-pressure of 430.1 mm., a difference probably within his experimental error.

In such cases, then, we cannot calculate the composition of the distillate as we did in case 1; but as is apparent from the above, the composition of the liquid distilled is constant, as is the temperature of boiling, so long as the two layers are present, independent of the amounts of the two constituents.

When but one layer remains, its behavior is similar to the liquid in class 3.

3. When the liquids mix in all proportions, or in general when there is only one layer of liquid, it is possible to make a complete separation of the constituents by a fractional distillation, if the vapor-pressures of all mixtures lie between the vapor-pressures of the pure constituents; for then the lowest boiling distillate will be that pure constituent which has the higher vapor-pressure.

If we use a system of coordinates in which the vapor-pressures are laid out upon the axis of ordinates, and the percentage composition of the mixture upon the axis of abscissas, we find that the vapor-pressure never reaches the sum of those of the constituents, but at times goes even below the smaller of these. The figure gives the three types of curves thus obtained, which will illustrate the principle involved. We find in I a maximum of the vapor-pressure corresponding to a certain strength of solution. In II this maximum has disappeared, and the vapor-pressure of every mixture lies between those of the pure constituents, while in III the opposite extreme to I is observed, i.e., a minimum of the vapor-pressure which corresponds to a certain composition.



I. Mixtures which correspond to this type possess a maximum of the vapor-pressure for a certain composition, i.e., the lowest boiling liquid is a solution of a certain strength. An example of this is a 75% solution of propyl alcohol in water. This 75% solution will distill at the lower temperature from any propyl-alcohol solution until one of the constituents, i.e., either the water or the propyl alcohol, has disappeared, when the other will remain behind in the almost pure state. Thus if we start with a 50% solution of propyl alcohol, a 75% solution will be distilled until all the alcohol is removed. and water alone is left in the flask. If we start with a 90% solution of the alcohol, the 75% solution will be given off until all the water has been used up, and pure propyl alcohol will remain behind.

II. For mixtures of this type we can make a complete separation by distillation. The vapor-pressure of all mixtures lies between those of the constituents; consequently the one with the higher vapor-pressure will be given off in the almost pure state, leaving the other behind. A solution of benzol in *m*-xylol falls in this class. The method of calculating the value of the vapor-pressure in such a case will be given later.

III. Here we have a minimum of the vapor-pressure corresponding to a certain composition. A solution of this composition will, then, always be the last to be distilled, since its boiling-point is the highest of all possible mixtures. This is just the opposite of case I, where the solution of a certain composition is given off first. All solutions, for example, of formic acid and water will distill off an amount of one constituent until the solution remaining contains 70% of formic acid. A 90% solution will give off almost pure formic acid until just enough remains to form a 70% solution. A 50% solution will give off water until the 70% solution is left behind.

It will be observed here that in cases I and III we find systems which behave as chemical individuals, or compounds (p. 147), i.e., the 75% solution of propyl alcohol in water, and the one containing 70% of formic acid. That these are chemical individuals in this respect only under this one condition, is proven by the fact that the composition of the vapor phase varies with the pressure under which the distillation takes place.

An interesting technical application of these principles and facts has been made by Young (Trans. Chem. Soc., 81, 707, 1902) in his method of preparing absolute alcohol from strong spirit. As is well known ethyl alcohol and water form a constant boiling liquid (B.P. = 78°.15) of a composition of 95.57% of alcohol and 4.43% of water, which by distillation alone cannot be further separated. Instead of employing a dehydrating agent and distilling the alcohol alone, as has been the common practice, he mixes with the solution benzene, *n*-hexane, or a similar liquid. The behavior of this system on distilling can be seen from the table below:

Liquid of Constant B.P.	B.P.	Percentage Composition.		
		Alcohol.	Water.	Benzene.
1. Alcohol, water and benzene....	64°.85	18.5	7.4	74.1
2. Alcohol and benzene..........	68°.25	32.41	....	67.59
3. Water and benzene............	69°.25	......	8.83	91.17
4. Alcohol and water............	78°.15	95.57	4.43	......
5. Alcohol......................	78°.3	100.0	......	......
6. Benzene......................	80°.2	......	......	100
7. Water........................	100°.0	......	100	......

The liquid of lowest boiling-point here is the ternary system water-alcohol-benzene, and, unless one liquid is present in a relatively very small quantity, it will distill first. If there is more than sufficient benzene to carry over the whole of the water, and if alcohol is present in excess, the ternary mixture will be followed by the binary mixture (alcohol-benzene), and the last substance to come over will be alcohol. Owing to the fact that there is but 3°.4 difference between the boiling-points of the ternary mixture, (water-alcohol-benzene), and the binary one (alcohol-benzene), however, it is impossible to get rid of all the water in one distillation. By redistilling the partially dehydrated alcohol once or twice with a further quantity of benzene, complete separation is effected. As the alcohol itself need not be distilled, but can be poured directly from the still, and as the benzene can be recovered without difficulty, this method has many advantages.

For further information on the distillation of liquids and liquid mixtures in general, see Young, Fractional Distillation, London, 1903.

We shall now consider the vapor-pressures of solutions of solids dissolved in liquids, where a change is caused in the vapor-pressure of the latter.

It has been known for many years that the vapor-pressure of a solution of a solid substance is lower than that of the pure solvent. Babo (1848) and Wüllner (1856) found, further, that *the depression of the vapor-pressure is proportional to the amount of solute present; and for the same solution the depression for any temperature is the same fraction of the vapor-pressure of the pure solvent.*

If p is the vapor-pressure of the pure solvent, p' that of the solution, and c the percentage of solute, then

$$\frac{p-p'}{p}=kc,$$

where k is the relative depression, $\frac{p-p'}{p}$, for a 1% solution.

Raoult in 1887 found experimentally that a more general relation is obtained if the relative depression is determined for 1 mole of substance in a certain amount of solvent. Thus he showed that all solutions containing one mole of substance in a certain weight of solvent possess the same vapor-pressure; i.e., *the* MOLECULAR *depression of the vapor-pressure is constant for all substances in the same solvent.* Further, he found that solutions of equi-molecular amounts of substance in equal weights of different solvents give relative depressions of the vapor-pressure which are proportional to the molecular weights of the solvents. *This shows that the vapor-pressure depends upon the relative number of moles of the solute and solvent.* We can contrast this with osmotic pressure, where the number of moles of dissolved substance per *liter* of solvent fixes the values.

Raoult summed up his results as follows: *One molecular weight of any substance dissolved in 99 moles of any solvent causes* *a 1% depression of the vapor-pressure.* (Here the number of moles of solvent is calculated from the gaseous molecular weight.) This, as will be seen, is a further definition for molecular weight in solution.

This law may also be expressed in another form: *The vapor-pressure of a solution is to that of the pure solvent as the number of moles of the solvent is to the total number of moles present in the solution, i.e., of solvent plus solute.*

For very dilute solutions the number of moles of the solute is so small in comparison with that of the solvent that the ratio becomes unity, i.e., the vapor-pressure of the solution is practically the same as that of the solvent.

Expressing the above laws as equations we obtain

$$\frac{p'}{p}=\frac{N_1}{N_1+N_2},$$

$$\frac{p-p'}{p}=\frac{N_2}{N_1+N_2},$$

and, further,

$$\frac{p-p'}{p'}=\frac{N_2}{N_1},$$

where N_1 is the number of moles of the solvent, and N_2 is the number of moles of the solute.

These equations will only hold when the solute is non-volatile, a condition which is practically fulfilled when its boiling-point, if it be a liquid, for which the same law would hold, is 140° above that of the solvent, and when N_2 represents the correct number of moles in solution. The value of N_1 here is the number of formula weights of solvent, i.e., the weight in grams divided by the molecular weight of *the solvent in the gaseous state;* N_2 of course being the weight of solute (in the solvent) divided by its molecular weight *in the solution.*

For the direct determination of the molecular weight it is more convenient to use the last form of equation given above, which may be expressed in words as follows:

The depression of the vapor-pressure is to the vapor-pressure of the solution as the number of moles of solute is to the number of moles of solvent.

Since $N_2=\frac{W_2}{M_2}$, where W_2 is the weight of solute in N_1 moles of solvent, and M_2 its molecular weight in the solution, and $N_1=\frac{W_1}{M_1}$, W_1 being the weight of solvent, and M_1 the molecular weight of *the solvent as a gas*, we have

$$\frac{p-p'}{p'}=\frac{W_2M_1}{M_2W_1}, \quad \text{or} \quad M_2=\frac{W_2M_1}{W_1}\cdot\frac{p'}{p-p'},$$

a relation which can be used as a laboratory method for finding the molecular weight of a substance in solution.

Example.—A solution of 2.47 grams of ethyl benzoate in 100 grams of benzene has a vapor-pressure of 742.6 mm., while pure benzene has one of 751.86 mm., both at 80° C. Find the molecular weight of ethyl benzoate. $W_2=2.47$, $M_1=78$, $W_1=100$, $p'=742.6$, $p=751.86$, $p-p'=9.26$; hence $M_2=154$, while from the chemical formula $C_6H_5COOC_2H_5$ we find $M=150$.

Biddle (Am. Chem. J., 29, 341, 1903) gives a differential method for determining the difference in vapor-pressures of pure solvent and solution (i.e., $p-p'$) for any concentration, and suggests calculating this to 1 mole of substance in 100 grams of solvent, and using it as the molecular depression of the vapor-pressure. In this way, of course, it is possible to determine molecular weights of other substances *in that solvent* by the use of a simple proportion. Thus we would find $(p-p')$ for 1 mole : $(p-p')$ found :: 1 : y, and y would represent the number of moles, i.e., $\frac{W_2}{M_2}$, contained in 100 grams of the solvent. Knowing the weight W_2, it is then easy to calculate M_2, the molecular weight from the calculated value of y.

Lewis (J. Am. Chem. Soc., 30, 668–683, 1908) calls attention to the fact that these laws of Raoult (with another mentioned later) are probably the most accurate we have for the behavior of substances in solution, for the van't Hoff osmotic pressure law gives absurdly low results for very high concentrations, and the Morse and Frazer modification (use of v_m as volume of solvent, in place of volume of solution, containing 1 mole), gives abnormally high values at very high concentrations. In fact, according to Lewis, osmotic pressures at very high concentrations can be more accurately determined indirectly from the vapor-pressure than is possible by direct measurement. For this purpose he derives the equation,

$$P-\tfrac{1}{2}\alpha P^2=\frac{RT}{v_m}\log_e\frac{p}{p'},$$

in which P is the osmotic pressure, α the coefficient of compressibility of the solvent, v_m its molecular volume (volume of 1 mole), and p and p' are respectively the vapor-pressure of pure solvent and solution. In other words, by substitution in the formula on page 171 of $\frac{p}{p'}$, for the molar fraction x.

When both solvent and solute are volatile it is still possible to calculate the vapor-pressure of the mixture under certain conditions. Here, as will be seen, we are returning to case 3, of liquid mixtures, page 156.

Since in such a case the vapor-pressure of each constituent is depressed by the other, we can find the total vapor-pressure, under ideal conditions, by subtracting from the sum of the vapor-pressures (i.e., assuming that neither affects the other), the sum of the effects of each on the other. We have then

$$p=p_1+p_2-\left(p_1\frac{N_2}{N_1+N_2}+p_2\frac{N_1}{N_1+N_2}\right),$$

where the sub-numerals distinguish the two constituents, the expressions $\frac{N_2}{N_1+N_2}$ and $\frac{N_1}{N_1+N_2}$ represent the *molar fraction* x, of each in the mixture, and the terms within the parenthesis being obtained from the equation $\frac{p-p'}{p}=\frac{N_2}{N_1+N_2}$, when written in the form $\Delta p=p\frac{N_2}{N_1+N_2}$, the value of p being that of the substance distinguished as N_1 in the equation. Considering each liquid in turn as solvent we find the effect of the other upon it to be $\Delta p_1=p_1\frac{N_2}{N_1+N_2}$ and $\Delta p_2=p_2\frac{N_1}{N_1+N_2}$.

Using $x=\frac{N_1}{N_1+N_2}$ and $1-x=\frac{N_2}{N_1+N_2}$, and rearranging, this formula becomes

$$p=p_1x+p_2(1-x),$$

where the two terms represent the partial pressures of the constituents *in the mixture*, or,

$$p=p_1'+p_2',$$

p_1' and p_2' being the partial pressures of each in the mixture (i.e., equal to p_1x and $p_2(1-x)$), p_1 and p_2 having represented the vapor-pressures at that temperature of the pure substances as measured alone.

Since by Dalton's law the total pressure is equal to the sum of the partial pressures, and these by definition (Avagadro's law) are dependent upon the number of moles in the gaseous space, N_1' and N_2', we have (see p. 39)

$$\frac{p_1'}{p}=\frac{N_1'}{N_1'+N_2'} \quad \text{and} \quad \frac{p_2'}{p}=\frac{N_2'}{N_1'+N_2'},$$

i.e., knowing the *partial pressure* of each constituent *in the mixture*, and the *total* vapor pressure of the mixture, we can find *the molar fraction* of each constituent *in the vapor*, $\frac{N_1'}{N_1'+N_2'}$ or $\frac{N_2'}{N_1'+N_2'}$, by dividing the partial pressure of each by the total pressure.

An example of the application of these relations in this simple form is given by a mixture of benzene and ethylene chloride at 49°.99 C. The sub-numeral 1 refers throughout to the benzene.

29.79 moles (i.e., x, molar per cent in the *liquid* state) of ethylene chloride, of which the vapor-pressure (p_2) is 236.2 mm. are mixed with 70.21 (i.e., $1-x$ molar per cent in the liquid state) of benzene, $p_1=268$ mm. What is the total vapor-pressure of the mixture? We find

$$p=268\times 0.7021+236.2\times 0.2979=258.42,$$

the observed value being 259 mm.

The molar fraction of each liquid in the *gases* distilling, then, is readily found by dividing the pressure of the constituent in the vapor by the total pressure. We have, then, for the molar percentages in the portion distilled,

$$\frac{N_1'}{N_1'+N_2'}=x'=\frac{268\times 0.7021}{258.42}=0.728$$

and

$$\frac{N_2'}{N_1'+N_2'}=1-x'=\frac{236.2\times 0.2979}{258.4}=0.272,$$

ie., the distillate from the solution containing 29.79 molar per cent of ethylene chloride and 70.21 molar per cent of benzene, contains 27.2 of ethylene chloride and 72.8 of benzene.

The law in this simple form has also been found to hold for such mixtures of liquids as the following: benzene-toluol; chlorbenzene-ethyl benzol-ethylene chloride-chloroform; ethylene bromide-propylene bromide.

In general the differential equation of Duhem-Margules,

$$\frac{d \log p_1}{d \log x} = \frac{d \log p_2}{d \log (1-x)},$$

in which x and $1-x$ are as above the molar fractions of the two liquids in the liquid mixture, holds for all cases of mixed liquids, so long as the liquids are miscible in all proportions. The general solution of this, as adopted by Zawidski gives

$$p_1' = p_1 x e^{\frac{\alpha_2}{2}(1-x)^2 + \frac{\alpha_3}{3}(1-x)^3},$$

$$p_2' = p_2(1-x) e^{\frac{\beta_2}{2}x^2 + \frac{\beta_3}{3} \cdot x^3},$$

where α_2 and α_3 are constants to be found from the partial vapor-pressure curves as observed for the specific liquids; and $\beta_2 = \alpha_2 + \alpha_3$; $\beta_3 = -\alpha_3$.

In those cases where x and β vanish, these equations naturally reduce to the ideal form

$$p_1' = p_1 x \ ; \ p_2' = p_2(1-x)$$

given above.

The distillation of ternary mixtures of liquids has been studied by Barrell, Thomas and Young (Phil. Mag., [5] **37**, 8, 1894) and very recently by Schulze (Jour. Am. Chem. Soc., **36**, 498, 1914). For further information on the above topic, in general, see Zawidski, Zeit. f. phys. Chem., **35**, 129, 1900; Gerber, Dissertation, Jena, 1904; Marshall, Trans. Chem. Soc., **89**, 1351, 1906; Latty, ibid., **92**, 1957, 1907, and Bose, Phys. Zeit., **8**, 353, 1907, and also Young's Fractional Distillation.

Increase of the boiling-point.—Since the vapor-pressure of a solvent is depressed by the solution of a substance in it, and the boiling temperature is that point at which the vapor-pressure becomes equal to one atmosphere, the boiling-point of a solvent must *increase* on the addition of a substance to it; so that from this term it will also be possible to define the molecular weight of the substance dissolved. It has been found empirically *that each mole of substance in solution increases the boiling-point of 1000 grams of solvent by an amount dependent only upon the nature of the solvent, and independent of the nature of the substance in solution. This constant we shall designate by the letter* $K_{\text{b.p.}}$.

The value of $K_{\text{b.p.}}$ for any one solvent can be found by experiment; or the existence of such a *boiling-point constant* can be readily shown, and its value calculated by the application of the second law of thermodynamics to the system.

Assume a very large amount of a solution in which there is 1 mole of substance to each 1000 grams of solvent.

To separate 1000 grams of pure solvent from this very large amount of solution by isothermal osmotic work at a constant osmotic pressure and at the boiling-point of the pure solvent, T, would require, by definition, the work equivalent to $2T$ cals., provided the heat of solution is negligible, i.e., that no heat need be added or removed during the process to retain the temperature constant at T, and provided the removal takes place against a constant pressure.

To transform this 1000 grams of liquid solvent into vapor at T from the pure solvent would now require 1000 l_e cals.

If this work of separation of solvent from the solution is to be done simply by the transformation of heat, it is quite evident that the heat must be absorbed at a higher temperature than T; i.e., to cause the complete separation to take place by boiling, the solution must boil at a higher temperature than the pure solvent, and just so much higher that the heat of evaporation of the pure solvent at T, 1000 l_e, can do the work $2T$ cals. We have then (p. 66),

$$\frac{2T}{1000l_e}=\frac{\Delta T}{T},$$

or

$$\Delta T_{\text{b.p.}}=\frac{0.002T^2_{\text{b.p.}}}{l_e}=K_{\text{b.p.}}$$

The boiling-point constant, the increase of the boiling-point of 1000 grams of any solvent due to the presence of 1 mole of substance in solution, is equal to 0.002 times the square of the absolute boiling-point of the solvent, divided by its heat of evaporation for 1 gram.

The value of this constant, $K_{\text{b.p.}}$, is *one-tenth of that of the conventional molecular increase of the boiling-point* (which refers to 1 mole in 100 grams), and is perhaps to be preferred, for it shows more clearly than that the limitations of the boiling-point law. It will be seen from the derivation that the law can only be expected to hold rigidly under the following conditions: (*1*) *the heat of concentration* (*negative heat of dilution*), *must be zero, or the solution so dilute as to make it negligible;* otherwise the osmotic work of separation will be larger or smaller than $2T$ cals. per mole; (2) *the pure solvent alone must vaporize from the solution, without admixture of solute;* and (3) *the solution must be so dilute that the gas laws hold, and* pv_m *really equals* RT.

Some of the values found by aid of this equation, which agree with those observed, are as follows:

INCREASE OF THE BOILING-POINT, $K_{b.p.}$

Solvent	$K_{b.p.}$ (1 mole in 1000 grams)
Water	0.52
Carbon tetrachloride	4.8
Chloroform	3.66
Methyl alcohol	0.88
Ethyl alcohol	1.15
Ether	2.10
Acetone	1.73
Benzene	2.57
Phenol	3.04
Carbon disulphide	2.37

while the values for other solvents will be found in Landolt-Börnstein-Roth, Tabellen, 1912, pages 757–800.

Naturally, in calculating $K_{b.p.}$ for a solvent for which, l_e, the heat of evaporation is unknown, we can substitute its value in other terms. Thus Innes (Proc. Chem. Soc., 18, 26–28, 1902) advocates the substitution for l_e of its value as given above (p. 94), $l_e=\frac{\Delta p}{\Delta T}\cdot\frac{2T^2}{pM}$, (i.e., from the Clapeyron-Clausius equation) and obtains

$$K_{b.p.}=\frac{0.002T^2}{\frac{\Delta p}{\Delta T}\cdot\frac{2T^2}{pM}}=\frac{\Delta T}{\Delta p}\cdot\frac{pM}{1000}.$$

$\frac{\Delta T}{\Delta p}$, here, is the change in boiling-point per unit change in external pressure, M is the molecular weight of the solvent *as a gas*, while p is the pressure at which T is the boiling-point. Of course Δp and p must be expressed in the same units.

Tsakalotos (C. r., 144, 1164–1106, 1907) substitutes for l_e

its value according to the Trouton-Nernst equation (p. 88, footnote) and finds

$$K_{\text{b.p.}} = \frac{M}{4750\frac{\log T}{T} - 3.5},$$

from which $K_{\text{b.p.}}$ can be calculated for any solvent simply from its boiling-point and molecular weight as a gas. It is also possible, of course, to substitute for l_e its value according to the Trouton-Bingham relation (p. 88). We obtain, then,

$$K_{\text{b.p.}} = \frac{M}{\frac{8500}{T} + 5.5}.$$

These two latter equations, however, will only give correct values for $K_{\text{b.p.}}$ when they give correct values for l_e, which they only do when the solvent is *non-associated.* It will be seen that in all these forms, we are using the fundamental equation, after substituting the theoretical value of l_e, in place of the experimental; so that there is no question in any case of a new fundamental principle.

In general the values of $K_{\text{b.p.}}$ found by experiment agree with those calculated by the relation

$$K_{\text{b.p.}} = \frac{0.002T^2}{l_e}.$$

It will be seen that any liquid can be used as the solvent in the boiling-point method, so long as it is not a solution, judged by the formation of a gaseous phase, i.e., *so long as the vapor it sends off when pure is of the same composition as the liquid it leaves behind.* (See Beckmann, Zeit. f. phys. Chem., 53, 129–137; and 58, 543–559.)

Knowing $K_{b.p.}$ for any liquid it is easy to calculate the increase of the boiling-point due to the addition of any small amount of substance dissolved in the solvent. All that is necessary is to find by a proportion from the data the number of moles of substance in 1000 grams of solvent, and then by another proportion to find the increase, from the known increase due to the presence of 1 mole in 1000 grams. Or, knowing $K_{b.p}$ and the increase, the molecular weight can be readily calculated.

Thus it is found that the addition of 2.0579 grams of iodine to 30.14 grams to ether causes an increase in the boiling-point of 0°.566. What is the molecular weight of iodine in ether? $K_{b.p.} = 2^{\circ}.10$.

The number of grams per 1000 grams is first found from the proportion

$$30.14 : 1000 :: 2.0579 : x.$$

Since M grams per 1000 grams would give an increase of 2°.10, M the molecular weight can be found from the proportion

$$x : 0.566 :: M : 2.10,$$

i.e., $M = 253$. Iodine in an ethereal solution, then, has the formula I_2; i.e., its formula or molecular weight in this solution is twice its atomic weight.

What is the increase of the boiling-point of 1.1 grams of sugar in 76 grams of water? $K_{b.p.}$ for water is 0.52.

Since the molecular weight of sugar in water solution is 342, we have the $\frac{1.1}{342}$ mole in 76 grams of water, or x moles in 1000 grams of water, where x can be found from the proportion

$$76 : 1000 :: \frac{1.1}{342} : x.$$

Then, since 1 mole of sugar in 1000 grams of water would increase the boiling-point 0°.52, our increase must be y in

$$1 : x :: 0.52 : y,$$

where $y = 0°.022$.*

We see here that the boiling-point increase due to substance added to a solvent depends upon the number of moles of solute to 1000 grams of solvent, and on the boiling-point, and heat of evaporation, of the solvent. Contrasting this with osmotic pressure, where only moles per liter and temperature, and with vapor-pressure, where only moles in moles of solvent and the vapor-pressure of the solvent are necessary, we see that it is somewhat more complicated than these.

Depression of the freezing-point.—More than one hundred years ago Blagden found by experiment that the freezing-point of a solvent is depressed by the addition of any substance to it.

Just as for the boiling-point increase it has been found empirically that *each mole of substance in solution depresses the freezing-point of 1000 grams of solvent by an amount dependent only upon the nature of the solvent, and independent of the nature of the substance in solution. This constant, which we shall designate by the letter* $K_{\text{f.p.}}$, can also be found either by experiment, or by a calculation based upon the second law of thermodynamics.

It can also be shown qualitatively and very simply that since the addition of substance to a liquid lowers its vapor-pressure, it must also lower its freezing-point.

Since the ice which is separated is the pure solvent, and the freezing-point is that temperature at which both solid and liquid may exist together in equilibrium in all proportions, the vapor-pressure of ice and liquid at the freezing-point must be the same. This has already been proven, and if it were not true a perpetual motion would be possible. In the figure, *ww* is the vapor-pressure curve for water, *ss* that for a solution, and *i* that for ice. At the point $t=0$, ice and water have the same vapor-pressure, and so are in equilibrium. The solution and ice, however, can only be in equilibrium at the temperature corresponding to the intersection of the two curves, *i* and *ss*, for only there will the vapor-pressures be the same; i.e., the freezing-point of the solution, where ice and solution can exist together in equilibrium, must lie below that of pure water. The more substance in the solution, the lower the vapor-pressure curve will be, and the lower consequently will be the point of its intersection with the ice curve, and the lower the freezing-point will lie.

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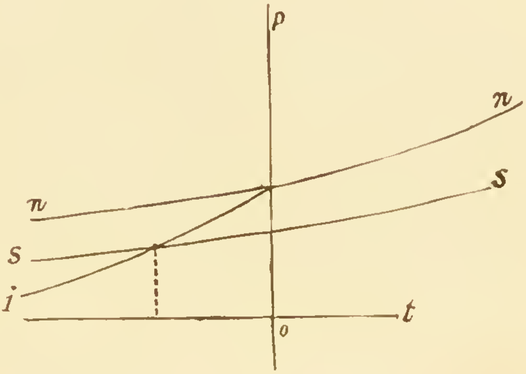
* The molecular weight or the increase of the boiling-point can also be found in one operation by aid of the equation $M = 1000 K_{\text{b.p.}} \frac{w}{W\Delta}$, where w represents the grams of substance, W the grams of solvent, Δ the increase, and M the molecular weight of the dissolved substance; but the above form will be found much easier to remember.



The quantitative relation between freezing-point depression and concentration of dissolved substance, can be derived just as was that for the boiling-point increase.

Assume a very large amount of a solution in which there is 1 mole of substance to each 1000 grams of solvent.

To separate 1000 grams of pure solvent from this very large amount of solution by isothermal osmotic work at a constant osmotic pressure and T°, the freezing-point of the pure solvent, would require, by definition, the work equivalent to $2T$ cals., provided the heat of the concentration taking place is negligible, i.e., that no further heat need be added or removed during the process of separation to retain the temperature constant at T.

The freezing of this 1000 grams of solvent would evolve at T 1000 l_f cals. In other words, the removal of 1000 grams of pure solvent from the solvent, by means of an isothermal crystallization, would evolve an amount of heat equal to 1000 l_f calories.

If now this work of separation of solvent *from the solution* is to be done simply by the transformation of heat, it is quite evident that the heat must be evolved at a lower temperature than T; i.e., to cause the complete separation by freezing out the 1000 grams from the very large amount of solution, the solution must freeze at a lower temperature than the pure solvent, and just so much lower that the heat of fusion, which is 1000 l_f at T, can do the work $2T$ cals. We have, then (p. 66).

$$\frac{2T}{1000 l_f} = \frac{\Delta T}{T},$$

or

$$\Delta T_{\text{f.p.}} = \frac{0.002 T^2_{\text{f.p.}}}{l_f} = K_{\text{f.p.}}$$

The freezing-point constant, the depression of the freezing-point of 1000 grams of any solvent due to the presence of 1 mole of substance in solution, is equal to 0.002 times the square of the absolute freezing-point of the solvent, divided by its heat of fusion for 1 gram.

The value of this $K_{\text{f.p.}}$ is also *one-tenth of the conventional molecular freezing-point* constant, just as our boiling-point constant was related to the conventional one, and given in this form also indicates more fairly and clearly the limitations of the method.

This law, from its derivation, can only hold rigidly under the following conditions: (1) *The heat of concentration must be zero, or the solution must be so dilute that this heat is negligible,* otherwise the osmotic work of separation will be larger or smaller than $2T$ cals.; (2) *the pure solvent, alone, must be separate from the solution as the solid phase;* and (3) *the solution must be so dilute that the gas laws hold in it, i.e.,* pv_m *must equal* RT. (See Bancroft, Jour. Phys. Chem., **10**, 319, 1906.)

Just as with the boiling-point, the values of $K_{f.p.}$ found by this equation agree in general with those experimentally determined.

Some of the values found for this factor are given in the table below:

DEPRESSION OF THE FREEZING-POINT, $K_{f.p.}$

Solvent	$K_{f.p.}$ (1 mole in 1000 grams).
Benzene	4.9
Phenol	7.3
Water	1.86
Acetic acid	3.9
Nitrobenzene	7.05

For the values for other solvents, see Landolt-Börnstein-Roth, Tabellen, 1912, pages 791–796.

It will be seen that any liquid can be used as the solvent in the freezing-point method so long as it is not a solution, judged by the formation of a solid phase, i.e., so long as the solid separating from the pure solvent has the same composition as the liquid it leaves behind. (See Morgan and Benson, Jour. Am. Chem. Soc., **29**, 1168–1175, 1907, and Morgan and Owen, *Ibid.*; **29**, 1439–1442, 1907, who used molten hydrated salts, of the type $CaCl_2 \cdot 6H_2O$ as solvent, solid $CaCl_2 \cdot 6H_2O$ separating in the pure state in every case.)

It is also simpler in calculating molecular weights from the freezing-point depressions to use two proportions rather than the formula usually employed.* What is the molecular weight of acetic acid in water? 0.681 gram in 100 grams of water causes a depression of the freezing-point of 0°.2168; $K_{\text{f.p.}}$ for water is 1.86.

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* $M = 1000\ K_{f.p.} \frac{w}{W\Delta}$, see p. 194, footnote.

Since there are 0.681 gram in 100 grams of water there must be 6.81 grams in 1000 grams of water, and we have

$$M : 1^\circ.86 :: 6.81 : 0^\circ.2168,$$

hence M the molecular weight of acetic acid in water solution is 58.4, in place of 60, the formula weight.

What is the freezing-point of 3.45 grams of glucose in 65 grams of water? The molecular weight of glucose is 180, and $K_{\text{f.p.}}$ for water is 1.86.

3.45 grams of glucose in 65 grams of water would be x grams in 1000 grams of water, where x can be found from the proportion

$$3.45 : 65 :: x : 1000.$$

We must have, then, $\frac{x}{180}$ moles of glucose in 1000 grams of water, and the freezing-point depression will be y in

$$1 : 1^\circ.86 :: \frac{x}{180} : y^\circ,$$

$$y = 0.^\circ 549.$$

Dawson and Jackson (Trans. Chem. Soc., **93–94**, 344–350, 1908) have shown that the *lowering of the transition temperature* of a solvent, i.e., the temperature at which one solid modification of the solvent is transformed into another, can also be used just as the freezing-point for the estimation of molecular weight in solution; as well as the molten hydrated salts having a *constant freezing-point*, mentioned above.

One point to be kept in mind here is that the freezing-point determined, when the solid phase is formed from the solution, is of a solution which is more concentrated than the one started with, for some of the solvent has been removed by the freezing. This follows from the fact that the freezing-point is that temperature at which ice and solution exist together in equilibrium. The concentration of the solution due to the separation of ice may be calculated from the overcooling (see p. 129), for it has been found for water that for each degree of overcooling 12.5 grams of water separates from each liter. Each degree of overcooling, then, causes the solution to be 1/80 more concentrated than the original one. If the solution is dilute, we may find the freezing-point of the original solution by a proportion. Thus if the overcooling is 1°, the depression of the freezing-point 0.1, and v represents the volume of solution, we have

$$v : (v - \tfrac{1}{80}v) :: 0^\circ.1 : x,$$

where x gives us the depression of the freezing-point caused by the solution of the weighed amount of substance in the volume v, i.e., in the volume of solvent present before the separation of solid. This, of course, is simply an interpolation on the assumption that the relationship, freezing-point to concentration, is linear for such small intervals.

Or, and this will hold for concentrated as well as dilute solutions, we may calculate from the overcooling the real strength of the solution in equilibrium with ice, i.e., the solution whose freezing-point we have actually determined (see also p. 129).

Thus in the illustrative example on page 198 suppose the overcooling had been 2°. Each degree would have caused the separation of 1/80 of the water present, consequently in this case, in place of really having 0.681 gram of acetic acid in 100 grams of water, we would have 0.681 gram in $(100 - 100\tfrac{1}{40})$ grams, which must be calculated to 1000 grams of water and then used in the proportion.

All these overcooling difficulties may be avoided by using the simple method proposed by T. W. Richards (Jour. Am. Chem. Soc., **25**, 291–298, 1902).

Here the temperature of a mixture of the solid and its pure liquid phase is noted after equilibrium has been established. Then a strong solution of the substance is added, the whole system, stirred, and the thermometer read again. By analyzing a sample of the liquid phase, withdrawn by a pipette from the vicinity of the thermometer bulb, the strength of the solution, of which the freezing-point depression has been read, is finally found. This method is especially valuable when by the Beckmann method the solid separated might contain solute as well as solvent.

Lewis (J. Am. Chem. Soc., **30**, 668–683, 1908) considers the freezing-point method to be even better than that depending upon vapor-pressure for the indirect determination of osmotic pressure. The formula he derives for this purpose for aqueous solutions is

$$P = 12.06\Delta - 0.021\Delta^2,$$

when P is the osmotic pressure in atmospheres and Δ is the depression of the freezing-point in centigrade degrees.

Just as with the boiling-point increase, the depression of the freezing-point of a solvent by the addition to it of substance depends upon the moles of substance in 1000 grams of the solvent, and upon its freezing-point and heat of fusion.

It must be borne in mind here that the freezing-point of a solvent is often raised by the addition of substance to it, but in such a case the solid phase separating, is not the one separating from the pure solvent. An example of this is shown in the addition of $CaCl_2$ to water, where, if a sufficient amount be added, ultimately $CaCl_2 \cdot 6H_2O$ will be formed, and the solution will exhibit a freezing-point, with $CaCl_2 \cdot 6H_2O$ as the solid phase, in the neighborhood of 30°.

It is also possible, naturally, to add substance to a solution and have its freezing-point either decrease or increase. Thus if the substances added do not react together, the addition of the second to the solution of the first will lower the freezing-point still further, or the two substances may react to form a smaller number of moles than were present of the first substance, when the freezing-point will rise. If the two substances unite to form 1 mole of a compound for every mole of original substance present, then the addition of the second to a solution of the first will leave the freezing-point of that unchanged. In all these cases, naturally, we are assuming the solid phase to be pure ice.

Electrolytic dissociation or ionization.—The molecular weights of a very large number of organic substances in water are found correctly from the osmotic pressure and the other methods mentioned above, i.e., they correspond to the values in the gaseous state. For other substances, however, varying results are obtained. The osmotic pressures, freezing-point depressions, boiling-point increases, and vapor-pressures are here always too large, and consequently from our definitions the molecular weight is smaller than that observed in the gaseous state. This reminds one immediately of the abnormal densities of gases. In the case of the gas the volume increases and the pressure is constant; in that of the solution, however, the volume must remain constant so the osmotic pressure increases.

Arrhenius, in attempting to find an explanation for the abnormal osmotic pressures, found by experiment that *those substances, and only those, which give abnormal osmotic pressures in solution are capable of conducting the electric current, and if they are dissolved in other solvents in which they behave normally they lose this power.*

Arrhenius determined the electrical conductivity of the substance in terms of equivalent conductivity. The equivalent conductivity of a solution being defined as the reciprocal of the resistance (in ohms) of the volume of liquid which contains one equivalent (hydrogen-value) weight of the substance, i.e., the weight of the generally accepted formula, divided by the valence, the electrodes being 1 cm. apart and large enough to contain between them the entire amount of solution. This value, naturally, is not found directly, but is calculated from that value found for a centimeter cube of the solution. (See Chapter IX.) In this way, always having 1 equivalent (according to the accepted formula) between the electrodes, he found that the more dilute the solution, the greater is the equivalent conductivity. In many cases, indeed, he was able to reach such a dilution that the equivalent conductivity attained a maximum value, which is unaffected by further dilution. This equivalent conductivity at infinite dilution, as it is called, is designated by the term Λ_∞, that value for any dilution v_e*, being designated by Λ_{v_e}.

From this it is apparent that the solution undergoes some kind of a change as the result of dilution; and the investigation of such solutions at various dilutions shows, indeed, that the molecular weight (according to definition) also changes with the dilution; the molecular weight decreasing to a minimum, constant, value, which, for binary electrolytes, is one-half the formula weight of the substance dissolved. It is not unreasonable, then, to infer that the breaking down of the formula (and consequently of its weight) of the substance in the solution is very intimately connected with the power it possesses of conducting the electric current.

These facts formed the starting point of what is known at present as the "theory of electrolytic dissociation."

As this theory is the subject of much speculation to-day it will be well for us to consider carefully just what in it is fact, and what, assumption, and to see clearly which portions are hypothetical, and which are destined to remain under any hypothesis, or lack of hypothesis; in other words, which are experimental facts. It may be said, however, that that which is hypothesis in this theory is unessential, as far as the use of the data is concerned, and the only hypothesis present, as we shall consider it, is that inherent in the terminology, which is carried over from the atomic hypothesis, and as such is beyond our power at present either to prove or disprove conclusively.

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* We have designated the volume of 1 mole by v_m, let us from now on designate the volume containing one equivalent by v_e.

The salient facts which have been grouped in this theory, for it is a theory in the sense that it is a law of nature holding between certain limits, although these are not as yet definitely fixed, are as follows:

(1) The equivalent conductivity of certain substances in water is found to increase up to a maximum, constant value, and this increase is the result of dilution.

(2) Those solutions which conduct the current also give abnormal osmotic pressures, freezing-points, boiling-points, and vapor-pressures; in other words, the molecular weight (according to the above definitions) decreases with increased dilution and finally reaches a minimum value, which, for binary electrolytes, is one-half the accepted formula weight of the substance.

(3) Those substances which in water conduct the current and give abnormal osmotic pressures, depressions of the freezing-point and vapor-pressure, and increases of the boiling-point, give normal osmotic pressures, etc., when dissolved in other solvents in which they do not conduct.

(4) The nearer the value of Λ_{v_e} is to that of Λ_∞, the more abnormal the value of the osmotic pressures, etc. (formula weight), of the solution. And the solution for which Λ_∞ is found also gives the maximum osmotic pressure, i.e., the minimum molecular or formula weight.

(5) The equivalent conductivity of a solution at infinite dilution is an additive value, i.e., is equal to the sum of the conductivities of the substances of which it is composed. The meaning of this is as follows: The equivalent conductivity at

infinite dilution of, for example, potassium chloride plus that of nitric acid minus that of potassium nitrate is found to be equal to that of hydrochloric acid. In other words,

$$\Lambda_{\infty KCl} + \Lambda_{\infty HNO_3} - \Lambda_{\infty KNO_3} = \Lambda_{\infty HCl}.$$

For this to be true, and it is true in general for all such substances, it is necessary that the equivalent conductivity of each substance in solution be the sum of two values which are independent each of the other. Chlorine, for example, as the constituent of an electrolyte, at the dilution giving Λ_∞, has the same conducting effect when part of the compound HCl as it has in KCl. It is possible, then, to find the value of Λ_∞ for any binary electrolyte when the values for the elements composing it are known. In other words, the conductivities of the solution as produced by the presence of any element can be calculated; and from these values, by summation, the value of Λ_∞ for any binary electrolyte can be found.

(6) When a solution is electrolyzed, the products of electrolysis appear instantaneously at the electrodes so soon as the circuit is completed. This indicates (since the solvent, water, does not conduct beyond a very small extent) that whatever does carry the current through the liquid is charged with electricity even before the current is applied, for the conduction is due to the dissolved substance, and the speed of movement of the substance has been measured and found to be so small, that it is no question of matter being electrically charged at one electrode before carrying this charge bodily through the solution to the other. (See Chapter IX.) Further, it is observed that the same amount of electricity, 96494 coulombs, which is called a Faraday, is necessary for the separation of one equivalent weight (in grams) of any element; in other words that 96494 coulombs of electricity are transported

through the liquid with each equivalent weight (in grams) of an element deposited. (Faraday's Law, see Chapter IX.)

(7) The properties of electrolytes are found to be the sum of the properties of the products produced by the electroylsis. Thus any solution giving off chlorine on electrolysis, excluding secondary reactions, will precipitate silver from its solution as the chloride. And if chlorine cannot be produced in any way by the electrolysis, silver will not be precipitated as chloride from its solutions. And, on the other hand, silver is only precipitated by chlorine, i.e., silver chloride is only formed in the solution, when it is contained in a solution from which silver can be deposited by the current by primary action.

The catalytic effect of weak acids on the inversion of sugar, as well as on the decomposition of methyl acetate, is found to be proportional to the ratio $\frac{\Lambda_{v_e}}{\Lambda_\infty}$ for the acid; and when a large amount of a salt of this acid is added to the acid this effect is decreased. But this is only true when the salt added is an electrolyte.

All copper solutions, when very dilute, show the same blue color, and this also depends upon the ratio $\frac{\Lambda_{v_e}}{\Lambda_\infty}$, and can also be changed, as the effect of acids were above, by the addition of a large amount of an electrolyte which contains the same acid radicle as the copper salt in question.

(8) Observation shows that when an element is separated on one electrode, anode or cathode, it is always separated on that one by primary action; in other words, the sign of the electricity transported by an element is always the same.* Unless an element in the pure state, when dissolved in water, reacts with the water it does not conduct the current. This circumstance is assumed to be due to the fact that only one kind of

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* See Le Blanc, Z. f. Electrochem., 11, 813-818, 1905.

electricity could be carried by the substance, and hence it produces no conduction.

The question now arises as to what theory can be found to correlate these facts and observations so that the generalization thus obtained may be employed to foresee other facts, and applied to other observations that they, in their turn, may be elucidated and generalized. By the word theory, then, we do not mean a hypothesis, in which something not observed is added to the facts to "explain" them, but only a generalization of observed facts. In other words, what law of nature, holding within definite, if narrow, limits, can be obtained from the above experimental facts when considered together?

The generalization which has been made from these facts is known as the theory of electrolytic dissociation, and, considering those portions which are free from hypothesis and fulfill the above conditions (in other words, omitting the hypothetical portions which it has attained since the time of its inception), we find in it, within certain limits, a definite law of nature.

The principal points of this theory are summarized below in brief form, and will each be expanded in the later portions of the book.

A substance in solution, which conducts the electric current, is dissociated or ionized into its constituents, and these constituents, when secondary actions are excluded, appear at the electrodes during electrolysis. The extent of the ionization or dissociation in any solution being given at the dilution v_e (number of liters in which 1 equivalent is dissolved) by the ratio

$$\frac{\Lambda_{v_e}}{\Lambda_\infty}=\alpha.$$

These products of ionization or dissociation are charged with electricity, 96494 coulombs being carried by the gram equivalent of any element (see (6) above). A further proof of this charged state of ionized matter is given by the fact that not only is the current carried by a solution dependent upon the number of gram equivalents deposited, but, as we shall see later, any other means of depositing the constituents of the solution upon the electrodes liberates an amount of electricity which depends also upon the number of gram equivalents deposited. And all electric batteries in order to give a current must contain electrolytes, i.e., solutions which are ionized.

Since a solution which by conductivity is shown to be completely ionized, or practically so, leads to a molecular weight, by osmotic pressure or any of the other methods, of one-half the value expressed by the formula weight, then, from the case of hydrochloric acid in solution, where

$$HCl \rightleftarrows H^{+} + Cl^{-},$$

the *formula weight of the hydrogen and chlorine in the allotropic, ionic state, according to our definition of molecular weight, must be synonymous with the atomic weight.* In this, ionic hydrogen and chlorine differ from gaseous hydrogen and chlorine, where the molecular weights are H_2 and Cl_2.

The ionic state, then, is an allotropic form of the ordinary state of the constituents, and often differs from that in molecular weight, and always in being charged with electricity, in having less energy than when in the gaseous state, and in always being transformed into the ordinary state on the loss of its charge of electricity.

Since the constituents in the case already mentioned, and in general in all cases, show a molecular weight (by the definition) which is the same as the atomic weight, it is possible to determine α, the degree of ionization, by osmotic pressure, etc., measurements, or from the average molecular weight of the substance in solution, as determined by osmotic pressure or any of the other methods. If, for example, we start with one formula weight of hydrochloric acid in a solution, and α moles of it are ionized, the total number of moles will consist of $(1-\alpha)$ of un-ionized HCl and α moles each of H^+ and Cl^- (where the signs indicate the electrical charges). The total number of moles in the volume of the solution will go then from 1 to $(1-\alpha)+2\alpha$, i.e., to $1+\alpha$, and the ratio of osmotic pressure when entirely un-ionized to that when partially ionized will be the same as this, i.e., as $1 : 1+\alpha$. In other words, if the formula weight in a certain volume *should* give the osmotic pressure P', it will give, when ionized to the extent α, the pressure $P=(1+\alpha)P'$. Since the number of moles (by definition) shown by the same weight is thus increased, the average molecular weight will be smaller, and we have as the relation between the two values of the molecular weight: $M'(1+\alpha)=M$, where the M refers to substance if it were un-ionized, i.e., is the formula weight of the substance, and M' is the average molecular, or formula, weight observed.

Just as with gaseous dissociation, the ionization of a solution is affected by the presence of one of the products of the dissociation, and later when we consider the quantitative effect of this for gases, we shall also consider it for solutions.

Owing to the fact that the dissociated constituents in a solution were called ions (in the Faraday sense of charged atoms), it has become common to speak of and to represent the ionized state as though it were characterized by an atomic structure; in other words, as if it existed as an accumulation of charged particles of infinitesimal size. As this is pure hypothesis, and cannot be either proven or disproven by direct experiment, *we shall only use the word ionization here in the sense that it is expressive of the relation* $\frac{\Lambda_{v_e}}{\Lambda_\infty}$, *i.e., we shall only use it in the sense* *of ionized matter, according to this definition, and as purely expressive of an experimentally determined fact.*

Summarizing our argument, the application of the experimental definitions of formula or molecular weight in solution (derived as given above) indicates that certain substances are decomposed in certain solvents, the fraction decomposed being α in the expressions $M'(1+\alpha)=M$ (according to any of the methods) and $\alpha=\frac{\Lambda_{v_e}}{\Lambda_\infty}$, and increasing with the dilution up to the value which, for binary electrolytes, gives $M=2M'$. In general, for other than binary electrolytes, we have just as on page 30,

$$[(1-\alpha)+i\alpha]M'=M,$$

where at the maximum dilution we have

$$i=\frac{M}{M'}.$$

That this is really the result of a decomposition, and not merely the failure in these cases of the definitions of formula weight in solution, is evidenced by the above facts and many others, given later. And that this ionized matter which is formed is electrically charged is also not to be doubted, as well from the above facts as from the general agreement of the results by electrical and other methods.

It is always to be remembered, then, that when we speak of ionization we mean something which can be defined in terms of experiment, and is free from hypothesis. And the same is true of ionized matter, so long as we do not assume for it a certain structure as might be natural from the all too common expressions " an ion " or " the ions." In order to avoid this difficulty we shall speak of copper ion, chlorine ion, etc., meaning simply an amount of ionized copper or of ionized chlorine, in preference to copper ions or chlorine ions.

Later we shall find that starting with this definition of ionized matter in a simple substance we can derive other experimental definitions, not only for ionization in general, but also for the amount of any one definite kind of ionized matter which is present with any number of other kinds.

One fact may be mentioned here which indicates what a very marked difference dilution makes in the behavior of a substance, and which decidedly supports the conclusions we have just drawn. Although hydrochloric acid is more volatile than hydrocyanic acid, it has been observed that from a mixture of the dilute acids (0.1 molar of HCl) it is possible to distill the HCN quantitatively, provided the dilution of the HCl is retained at about this value by the frequent replacement of the water lost. In the light of the above theory the difference between the two acids in solution is that while $\frac{\Lambda_{v_e}}{\Lambda_\infty}$ is nearly equal to 1 for HCl, it is very small for HCN. In other words, HCl is composed principally of the ionized constituents H^+ and Cl^-, which cannot produce HCl gas without first going through the state HCl in solution, and that is prevented by the nearly constant dilution which is retained during the distillation. Any gaseous substance, then, which in solution is largely ionized, is more difficult to distill than an un-ionized or less ionized one. The HCN, being dissolved and retained in this state in solution, can be expelled readily just as any other gas which undergoes no great change in solution. This method, indeed, was discovered as the result of such theoretical reasoning, and it is but one example of the many practical applications of the above generalization. (For details of the separation, see Richards and Singer, Am. Chem. J., 27, 205, 1902).

It is not to be imagined that the facts mentioned above are the only ones leading to these conclusions, for later, throughout our work, we shall find occasion to consider other things which will confirm each of the steps leading to the final conclusion. In other words, it is not to be thought that the whole theory has been described in this place, or that, because some of the points mentioned are not clear, the theory itself is to be condemned, for many of the points can only be brought out after considering certain other methods which will enlarge our horizon. It may be said, however, that these further aids but confirm and make more evident the truth of the conclusions we have arrived at. At the same time we must not forget that we have been speaking of this subject as lying within certain limits, and so cannot expect our conclusions to hold outside of them, nor to condemn them because they do not. The relation of substances in non-aqueous solvents to a certain extent is different, and consequently these conclusions could not be expected to hold. As a matter of fact, the conduction relations for these solutions are so utterly different from the aqueous ones that it would be impossible to consider them together at all in the light of our present knowledge. All of these points will be discussed more fully later, however, and the limits stated, within which our conclusions in general will hold. It is to be remembered, however, that simply because our theory does not hold for solutions in certain non-aqueous solvents (solutions which show no similarity in behavior to the aqueous ones, and which may or may not be solutions, as we consider them, but may involve an entire rearrangement of the composition of the solvent, or solute, or both), it should not be considered as false and of little use. For the two kinds of systems are so different that it would be impossible to imagine that both are subject to the same laws.

The value for α, the degree of ionization for a few electrolytes of various types is given below for varying conditions. (Noyes and Johnston, Jour. Am. Chem. Soc., 31, 987–1010, 1909). These are the values as found from the ratio of equivalent conductivities, since that method is the most delicate one for this purpose which we possess.

VALUES OF α, THE PERCENTAGE OF IONIZATION

Potassium Nitrate (1—1).

Concentration Milli-equivalents per Liter.	0°.	18°.	25°.	50°.	75°.	100°.	128°.	156°.
2.0	97.3	97.0	96.9	97.2	97.0	96.4	95.0	94.0
12.5	93.0	92.8	93.0	92.7	92.5	91.5	89.8	89.7
50.0	87.5	86.8	87.1	86.6	86.2	85.0	83.1	82.1
100.0	83.1	82.8	82.9	82.4	81.8	80.4	78.4	77.2
Potassium Oxalate (1—2).								
2.0	94.5	94.0	94.5	93.9	93.1	92.9	90.9	89.9
12.5	87.3	87.2	87.7	86.7	85.4	84.5	81.7	80.4
50.0	79.4	79.2	79.1	77.8	76.0	74.5	71.4	68.9
100.0	74.7	74.3	74.3	72.6	70.6	69.0	65.6	62.8
200.0	70.3	69.5	69.5	67.4	65.5	63.2	59.9	57.0
Calcium Nitrate (2—1).								
2.0	94.4	95.0	94.6	95.0	94.6	93.7	92.5	92.2
12.5	86.4	87.6	87.6	87.3	86.5	85.3	83.1	82.4
50.0	78.9	78.8	78.5	77.8	76.7	75.0	72.3	70.4
100.0	73.7	73.5	73.3	72.3	71.0	69.2	66.5	64.2
200.0	68.7	68.3	68.0	67.0	65.5	63.5	60.8	58.3
Potassium Ferrocyanide (1—4).								
0.5	93.2	....	92.2					
2.0	86.3	85.8	85.8	84.5	83.1	81.2		
12.5	72.2	71.0	71.0	69.4	67.2	64.5		
50.0	59.2	58.7	58.6	56.7	54.5	51.6		
100.0	53.9	53.2	53.0	51.3	49.1	46.5		
200.0	49.6	48.8	48.6	47.1	44.8	42.1		
400.0	46.2	45.3	45.0	43.3	41.1	38.5		
Calcium Ferrocyanide (2—4).								
2.0	53.5	51.7	50.4	48.0				
12.5	35.5	34.2	33.6					
50.0	27.4	26.4	26.0	23.8	21.2			
100.0	24.9	24.0	23.5	21.6	19.1	16.5		
200.0	23.4	22.5	22.1	20.3	17.8	15.1		
400.0	23.0	22.1	21.7	19.9	17.5	14.9		

POTASSIUM CITRATE (1 – 3).

Conc. Milli-equivalents per Liter.	0°.	18°.	25°.	50°.	75°.	100°.	128°.	156°.
0.5	....	96.4	96.4					
2.0	93.0	92.6	93.0	92.0	92.0	90.8		
5.0	88.6	88.2	88.7	87.3	86.5	85.0		
12.5	82.4	81.7	82.1	80.5	79.4	77.7		
50.0	71.3	70.4	70.7	69.1	67.4	65.0		
100.0	65.7	64.8	65.0	63.0	61.4	59.0		
300.0	57	56.0	56.0	54.2	52.2	50.0		

LANTHANUM NITRATE (3 – 1).

Conc. Milli-equivalents per Liter.	0°.	18°.	25°.	50°.	75°.	100°.	128°.	156°.
2.0	91.4	90.4	90.4	89.9	89.5	88.1	85.6	84.3
12.5	81.6	80.4	80.4	79.2	77.7	75.3	71.8	68.8
50.0	71.6	70.2	70.0	68.3	66.3	63.3	59.2	55.0
100.0	66.3	64.7	64.4	62.5	60.5	57.3	53.0	48.6
200.0	61.0	58.8	58.6	56.7	54.4	51.1	46.7	42.4

TETRA-SODIUM BENZENE-PENTA-CARBOXYLATE * (1 – 4).

Conc. Millimoles.	0°.	25°.	50°.
0.2	88.7	90.1	89.3
0.6	82.5	83.9	82.9
2.0	73.2	74.2	72.9
6.0	63.6	64.2	62.9
20.0	53.4	54.3	53.1
50.0	47.0	48.1	47.1

PENTA-SODIUM BENZENE-PENTA-CARBOXYLATE * (1 – 5).

Conc. Millimoles.	0°.	25°.	50°.
0.2	87.8	85.2	83.5
0.6	80.0	77.2	75.1
2.0	68.1	65.5	63.6
6.0	57.2	55.0	52.8
20.0	47.2	45.6	43.1
50.0	41.3	40.3	38.7

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* Noyes and Lombard, J. Am. Chem. Soc. 33, 1433, 1911.

Certain general relations have been observed connecting the extent of the ionization of salts of the same type, and also connecting the ionization of salts of different types, which are very convenient approximations. We regard salts as of the same type, here, when they produce ions of the same valences. Thus if two monovalent ions are formed in solution, we say the salt is *uni-univalent* (1 – 1); when two monovalent ions and one divalent ion are produced we call the salt *uni-bivalent* (1 – 2); and in the same way we have *uni-trivalent*, (1 – 3); *uni-tetravalent* (1 – 4); *uni-pentavalent* (1 – 5); and *uni-hexavalent* (1 – 6). When two divalent ions are formed we have, naturally, a *bi-bivalent* (2 – 2) salt and, finally, when we have three divalent ions and two trivalent the salt is *bi-trivalent* (2 – 3), and, in the same way, for two bivalent ions and one tetravalent ion we have *bi-tetravalent* (2 – 4). Here it makes no difference whether it is the positive or negative ion which has the higher valence, a salt designated as (2 – 4) being identical, as far as type is concerned, with one designated as (4 – 2).

A. A. Noyes and his co-workers have shown that *salts of the same type have ionization values, at the same concentration and temperature, which do not differ from one another by more than a few per cent*—in other words, *the degree of ionization of salts is primarily determined by the ionic type.* Further, *for salts of differing types, there is an approximate proportionality* existing between the *percentage* UN-IONIZED *and the valence product*, and this is true whether the comparison is made at *equimolar* or at *equinormal* (equivalent) ion concentrations, *but more nearly so for equimolar concentrations.* This rule seems to hold with as great a degree of accuracy as the one above concerning salts of the same type.

The experimental evidence for the above rules is given in brief by the following tables, taken from the original papers, and presented in such form as to be readily comprehended.

IONIZATION IN RELATION TO VALENCE TYPE

Salt.	Valence Product.	Percentage Ionized.					
		Salt Concentration 0.1 M.		0.05 Eq. per Liter		0.05 Moles per Liter.	
		18°.	100°.	18°.	100°.	18°.	100°.
KCl	1×1	86	81	89	83	89	83
KNO_3	1×1	83	80	86	84	86	84
NaCl	1×1	84	82	87	85	87	85
$AgNO_3$	1×1	81	79	85	82	85	82
$NaC_2H_3O_2$	1×1	79	75	83	80	83	80
Mean	1	83	80	86	83	86	83
K_2SO_4	1×2	72	69	75	68	68	61
$K_2C_2O_4$	1×2	74	69	78	73	72	66
$Ca(NO_3)_2$	2×1	73	69	77	73	72	66
$Ba(NO_3)_2$	2×1	68	66	71	69	64	62
Mean	2	72	68	75	71	69	65
$K_3C_6H_5O_7$	1×3	65	59	67	61	57	50
$La(NO_3)_3$	3×1	65	57	67	58	56	47
Mean	3	65	58	67	60	57	49
$MgSO_4$	2×2	45	31	43	28 *	36	24 *
$K_4Fe(CN)_6$	1×4	53	46	53	46	45	37
$La_2(SO_4)_3$	3×2	17	7	10 *	5 *	10 *	5 *
$Ca_2Fe(CN)_6$	2×4	24	16	23	14 *	21	14 *

* Relatively inaccurate values.

According to these rules, then, we can find the approximate ionization of a salt of any type from figures for another of that type, or if that is not at hand, can find it from a salt of a simpler type; for example, by the proportion, using the types, $1-1$ and $(1-3)$ at 0.1 molar,

$$(1-\alpha)_{1-1} : (1-\alpha)_{1-3} :: 1\times1 : 1\times3,$$

RELATION OF UN-IONIZED FRACTION TO VALENCE-PRODUCT

Valence Product v_1v_2.	At Equimolal Ion-concentrations =0.05.				At Equinormal Ion-concentrations =0.05.			
	$100(1-\alpha)$.		$100(1-\alpha)/v_1v_2$		$100(1-\alpha)$.		$100(1-\alpha)/v_1v_2$	
	18°.	100°.	18°.	100°.	18°.	100°.	18°.	100°.
1×1	14	17	14	17	14	17	14	17
2×1	31	35	16	18	25	29	13	15
3×1	43	51	14	17	33	40	11	13
4×1	55	63	14	16	47	54	12	14
2×2	64	76	16	19	57	72	14	18
3×2	90	95	15	16	90	95	15	16
4×2	79	86	10	11	77	86	10	11

At 25°, 0.05 formal (i.e., molal or molar)

v_1v_2.	1×1.	2×1.	3×1.	4×1.	5×1.	2×2.
$1-\alpha$	0.135	0.28	0.39	0.52	0.60	0.58 *
$(1-\alpha)/v_1v_2$	0.135	0.14	0.13	0.13	0.12	0.145

* Average value for the sulphates of magnesium, zinc, and copper. This table is from Noyes and Lombard, J. Am. Chem. Soc. 33, 1435, 1911.

the designation of the salt, (1 – 1), (1 – 2), (1 – 3), (2 – 4), etc., giving the numbers to be used in finding the valence product $v_1 v_2$.

Another and similar relation to this is given by Bodländer, with Storbeck and Eberlein (Zeit. f. anorg. Chem., 31, 19, and 39, 195). According to this the ionization of any salt is equal to that for a 1 – 1 salt, *at the same* EQUIVALENT *dilution, raised to a power equal to the product of the valences of the ions of the salt whose ionization is to be determined.*

Examples of this relation are given in the tables below, all dilutions being *equivalent normal.*

Dilution (Liters per Equivalent).	100.	20.	10.	2.
α-ionization of KCl	0.94	0.88	0.85	0.78
α^2	0.88	0.77	0.73	0.61
Ionization of $BaCl_2$	0.87	0.77	0.74	0.60

Liters per Equivalent.	KCl.	Na_2SO_4.		$K_3Fe(CN)_6$.		$K_4Fe(CN)_6$.		$Na_6C_{12}O_{12}$.	
	α.	α'.	α^2.	α'.	α^3.	α'.	α^4.	α'.	α^6.
32	0.90	0.81	0.81	0.75	0.74	0.67	0.67	0.50	0.55
64	0.93	0.86	0.87	0.80	0.80	0.74	0.74		
128	0.95	0.90	0.90	0.85	0.85	0.81	0.81	0.65	0.73
256	0.96	0.92	0.92	0.89	0.89	0.87	0.87		
512	0.97	0.94	0.94	0.92	0.92	0.91	0.89	0.74	0.83
1024	0.98	0.96	0.96	0.95	0.94	0.94	0.93	0.89	0.89

Here α' is the actually determined value; α^2, α^3, α^4, and α^6 being the values of α for KCl raised to a power in each case equal to the product of the valences of the ions formed from the salt. Thus we have $2Na^+$ and SO_4^{--} (1×2); $3K^+$ and $Fe(CN)_6^{---}$ (1×3); $4K^+$ and $Fe(CN)_6^{----}$ (1×4); and finally $6Na^+$ and $C_{12}O_{12}^{------}$ (1×6); the concentrations for the 1/32 normal (equivalent ion concentration, i.e., per unit electrical charge) being $\frac{1}{2}(1/32Na_2SO_4$; $\frac{1}{3}(1/32K_3Fe(CN)_6)$; $\frac{1}{4}(1/32K_4Fe(CN)_6)$; and $\frac{1}{6}(1/32Na_6C_{12}O_{12})$. Whether this relation holds at other temperatures and for other salts is apparently not as yet known; certainly its results, however, are not always in accord with those based upon the better experimental material of Noyes, from which the simpler relation given above was derived. Using this law in the illustration above to find the ionization of a $(1-3)$ salt from one of the $(1-1)$ type, we would have at the same *equivalent* dilution

$$\alpha_{1-3} = \alpha_{1-1}^{3\times1}$$

The relations existing between osmotic pressure, vapor pressure, freezing-point and boiling-point, and the effect of ionization upon these quantities.—Although it is possible to find mathematical relations connecting the osmotic pressure with the vapor-pressure, or freezing-point, etc., it will be seen that any one of them may be found from any other by calculating back, from the given value, the concentration in moles per liter of the solution; for any of the values can be calculated when the concentration of solute is known. Thus the freezing-point of a water solution is 0°.3 below that of the pure solvent. What is the vapor-pressure of the solution at 0°, the vapor-pressure of pure water at 0° being 4.57 mm.?

Since 1 mole per 1000 *grams* of solvent would depress the freezing-point 1°.86 $(=K)_{\text{f.p.}}$ this solution must contain

$$1^\circ.86 : 0^\circ.3 :: 1 : x,$$

x moles per 1000. The vapor-pressure then, from $\frac{p'}{p}=\frac{N_1}{N_1+N_2}$, is

$$p'=4.57\,\frac{\frac{1000}{18}}{\frac{1000}{18}+x}\,\text{mm.},$$

for 1000 grams of water is equal to $\frac{1000}{18}$ moles.

When a depression of the vapor-pressure is given, i.e., $p-p'$ in the formula $\frac{p-p'}{p}=\frac{N_2}{N_1+N_2}$ or $\frac{p-p'}{p'}=\frac{N_2}{N_1}$, all we can find is the relation between the number of moles of solute (N_2) and those of solvent (N_1). But by fixing the amount of solvent, 1000 grams, for example, and knowing its molecular weight as a gas, we can solve the equation for the concentration of solute in that quantity of solvent, and then from this calculate the osmotic pressure, freezing-point or boiling-point of the solution.

Thus the vapor-pressure of a solution is $\frac{9}{10}$ that of the pure solvent (water) at 0°, what is the freezing-point depression of the solution? Since $\frac{p'}{p}$ in $\frac{p'}{p}=\frac{N_1}{N_1+N_2}$ is equal to 0.9, we have

$$0.9=\frac{N_1}{N_1+N_2}=\frac{\frac{1000}{18}}{\frac{1000}{18}+N_2},$$

where N_2 is the number of moles of solute in 1000 grams of solvent. The depressions of the freezing-point is therefore $N_2 \times 1^{\circ}.86$.

It now simply remains for us to express analytically the effect of ionization upon the osmotic pressure, depressions of the freezing-point and vapor-pressure, and increase of the boiling-point; for the definitions of formula weight in terms of these methods have already been stated, and the derivation of the concept of ionization traced from them.

Naturally, if in place of N moles per liter of solvent we have after ionization $N[(1-\alpha)+i\alpha]$, where i is the number of moles of ions formed from 1 mole of salt by complete ionization, the osmotic pressure can be found from the proportion

$$N : N[(1-\alpha)+i\alpha] :: N\left(22.4\frac{273+t}{273}\right) : P',$$

where P' is the osmotic pressure at t° of the N moles in 1 liter of solvent, ionized to the extent α into i ions.

The freezing-point depression is $\Delta_{\text{f.p.}}$ in the proportion

$$N : N[(1-\alpha)+i\alpha] :: NK_{\text{f.p.}} : \Delta_{\text{f.p.}},$$

where N and $N[(1-\alpha)+i\alpha]$ refer to moles per 1000 grams of solvent.

The boiling-point increase is $\Delta_{\text{f.p.}}$ in the proportion

$$N : N[(1-\alpha)+i\alpha] :: NK_{\text{b.p.}} : \Delta_{\text{b.p.}},$$

when N and $N[(1-\alpha)+i\alpha]$ also refer to moles per 1000 grams.

And the vapor-pressure is p' in the relations (using N_2 here for N above, to distinguish it from the moles of solvent, N_1),

$$\frac{p-p'}{p}=\frac{N_2[(1-\alpha)+i\alpha]}{N_1+N_2[(1-\alpha)+i\alpha]},\quad \frac{p-p'}{p'}=\frac{N_2[(1-\alpha)+i\alpha]}{N_1},$$

or

$$\frac{p'}{p}=\frac{N_1}{N_1+N_2[(1-\alpha)+i\alpha]},$$

where $N_1=\frac{1000}{M}$, M being the molecular weight of the *solvent as gas.*

At complete ionization into two ions, then, the osmotic pressure, depression of the freezing-point, and increase of the boiling-point would all be doubled, while the vapor-pressure would only be effected indirectly by the value of the term N_2 being doubled.

Solid solutions.—Solid solutions, which have already been considered in the previous chapter, are homogeneous solid phases which can vary continuously within certain limits. These limits are smaller for solids than they are for liquids, just as the limits for these are much more restricted than for gases. The most important differences between a solid solution and a mixture of solids are as follows: Work is necessary to separate the constituents of the solution, and consequently these do work in uniting to form the solution; a solution has a lower vapor-pressure than the pure solvent; and a solution has a smaller solubility in all liquids than the pure solvent. Examples of solid solutions are given by mixtures of isomorphous crystals; zeoliths, i.e., natural water-holding silicates, which lose water and yet retain their transparency, although the vapor-pressure is reduced; hydrogen with palladium; hydrogen with iron; and mixtures of two crystalline substances which have different forms, but which give a mix-crystal like that of the substance present in excess. The reader must be referred for further information on this subject to one of the books treating it in detail, Findlay's Phase Rule, for example.

Colloidal solutions, or dispersed systems.—In the previous pages, we have been discussing systems which could not, by any means in our power, be recognized as anything but homogeneous; even though the atomic or molecular hypotheses would regard them as non-homogeneous, i.e., as composed of two or more different kinds of molecules. In other words, it is impossible, experimentally, in those cases to find any trace even of non-homogeneity. There are other systems, however, and these have been studied very extensively in the past few years, which not only have quite different properties from the solutions we have been discussing, but which can also be shown by some of the newer methods developed to be decidedly non-homogeneous in structure — and therefore not true solutions according to the definition on page 147. These systems, characterized by the fact that the substance is dispersed throughout the liquid in actual particles, as can be proven experimentally, are called *colloidal solutions* or *dispersed systems.* The substances in solution in such systems differ from those we have been considering chiefly (in addition to failing to follow the above laws) in that they do not dialyze through parchment or parchment paper, and further in that they diffuse through the liquid space less rapidly than the others.

Von Weimarn and Wo. Ostwald (Koll. Zeit., 3, 26, 1908), classify the possibilities, with respect to the degree of dispersion, of a substance in solution, and at the same time show how such systems merge almost imperceptibly with those which are to be regarded as experimentally homogeneous, and which obey the laws we have discussed above, in the following way:

DISPERSOIDS

I. COARSE DISPERSIONS (suspensions, emulsions, etc.)
   Magnitude of particles, greater than 0.1μ[*]

II. COLLOIDAL SOLUTIONS
   Magnitude of particles from 0.1μ to $1\mu\mu$.
   Decreasing degree of colloidal behavior with increasing degree of dispersion.

III. MOLECULAR OR IONIC DISPERSOIDS.
   Magnitude of particle about $1\mu\mu$ or smaller.

The actual existence of particles in coarse dispersions or in colloidal solutions can be proven here either by aid of the microscope or of the ultramicroscope, and also very simply by the appearance of a so-called "Tyndall cone" in the system, when a powerful ray of light is sent through it. Here the cone is visible, just as a ray of sunlight in a darkened room is visible when passing through dust-laden air, and only then. In both cases, then, we prove the presence of discrete particles (i.e., the lack of optical homogeneity) from the fact that the light is only visible when particles are present. (For a discussion of the appearance of the Tyndall cone in solutions within the limit of our definition on page 147, see Le Blanc, Zeit. f. Elektrochem., **19**, 794–796, 1913.)

On examining dispersed systems whose particles can be proven to exist by the microscope or ultramicroscope, and which are smaller than 1μ, it is observed that the particles are always in rapid oscillatory motion, and that as the particle decreases in size, the rapidity of its motion increases. This continual motion of the particles is known as the *Brownian movement* (see Perrin, Brownian movement and molecular reality).

Such solutions as the above do not follow the laws already given for the behavior of homogeneous solutions, for the substance contained in dispersed form hardly affects at all the freezing-point, boiling-point or vapor-pressure of the solvent, and gives rise to such small osmotic pressures as to be almost negligible—and all this is true even when the substance exists to a considerable concentration in the solvent. The electrical behavior also of dispersed systems, i.e., their behavior on the passage through them of an electric current, is quite different from those we have already studied. In dispersed systems the action of the current is usually to separate the dispersed particles at one of the electrodes, according as to whether they were originally charged positively or negatively; this process is known as *cataphoresis*.

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[*] $\mu = 10^{-6}$ meter; $\mu\mu = 10^{-9}$ meter.

By mixing together two dispersed systems, one of which contains particles which are positively charged, and the other negatively—both with respect to the solvent—we observe a complete separation of the dispersed materials which were present, and the production of pure solvent. And in such a case we can go still further in the proof that the particles themselves are charged differently from the solvent, for it is observed that any electrolyte (i.e., any substance which produces charged ionic matter in the solution) will also cause the separation of the dispersoid. The power of an electrolyte to separate a colloidal system into its constituents is found here to depend upon the charge of the ion opposite in sign from that on the particle to be separated, and the greater the charge on the ion, the greater its coagulating effect. In general here emulsoids are not as sensitive as suspensions to the effect of electrolytes added.

Substances forming colloidal solutions can be distinguished as *reversible* (emulsoids) and *irreversible* (suspensoids); the reversible ones after coagulation going back into colloidal solution readily, while the others require special methods to put back into solution. The action of a reversible colloid present in an irreversible system will tend to inhibit the coagulating effect of an electrolyte upon the latter—this is called the action of *a protective colloid*. Thus in photography the presence of gelatine (a reversible colloid) causes silver chloride (an irreversible colloid) to remain colloidal and dispersed, even in the presence of electrolytes.

It is evident of course that the process of dispersion would increase enormously the surface of the substance exposed to the liquid, over what would be exposed if the substance were present as a lump. This fact makes the process of *adsorption*, the *effect of the surface of one substance* upon another substance of very great importance in colloid chemistry. This property is to be distinguished from the *volume* phenomenon known as *absorption*. The process in general of the reaction between a solid and a liquid is known as *sorption*, which is then subdivided into the two groups according as the action takes place only on the *surface* (adsorption) or throughout the mass (absorption).

The above very brief sketch simply considers some of the most fundamental ideas of colloid chemistry, and is given, not so much to illustrate the properties of dispersed systems, but to call further attention to those systems in which the general laws of solution hold, and to the limits set upon the application of these laws by our original definition of solution. For information on that vast, new branch of chemistry, colloid chemistry, the reader must be referred elsewhere. (See Zsigmondy-Alexander, Colloids and the Ultramicroscope, 1909, and Wo. Ostwald, Kolloid-Chemie, Leipzig, 1912.)

The molecular weight in solution.—Our definitions of molecular weight in solution (osmotic pressure, vapor-pressure, freezing-point and boiling-point) in general lead us to the same results when it is possible to equalize the experimental error and employ all methods. We have found, however, that in some cases the molecular weight so determined is very much smaller than the formula weight (dissociation), and in other cases several times larger than the formula weight (association).

Further, two associated liquids (according to definition by surface-tension) when mixed often show a mutual dissociation of the associated state. But these cases, excepting the last, are also found in connection with the molecular weight in the gaseous state, as it is affected by temperature changes, etc. It is not a question here of any difficulty with our definition of molecular weight, for the various methods seem to agree very well, and it is generally conceded that the various results express the molecular weight as it changes from solvent to solvent, and in the same solvent from dilution to dilution.

Certain results are found by the freezing-point method for both electrolytes and non-electrolytes, however, which are hard to follow so accurately by other methods, that are difficult to explain other than by assuming that there exists a hydration of the substance in solution. The freezing-point depression, in other words, is found to be greater than it should be from results calculated from data for more dilute solutions. The effect of this hydration would be small as to the increase in the molecular weight due to the addition of water; it is the solvent which is removed which would exert the greater influence upon the result, especially on the small amount present in concentrated solutions. By plotting actually observed results and assuming water to be removed from the solvent and to unite with the substance, a curve can be found which will be in accord with the law. In this way it is proven that *if* a hydrate were formed in the requisite extent, the law would be followed.

All the methods given above seem to give explicable results for very dilute solutions; the difficulties will be discussed later. For concentrated solutions, however, it is quite evident that the correct relations have not been obtained as yet. Whether the behavior of very concentrated solutions can ever be brought into accord with the more dilute ones is a question which is still open. It is obvious, though, notwithstanding the difficulties which have arisen, that the theory of solution is a law of nature holding between certain limits, and that the problems in this connection for the future have all to do with enlarging these limits. That this can only be done by following the results closely and avoiding all hypotheses is an opinion which is growing not alone in this branch of science, but in all others. To do this, however, it is not necessary to cast aside what we have learned, thinking it hypothesis, but to use the fragment of a great law of nature which we undoubtedly have in the theory of solution as a basis for further development.

CHAPTER VII

THERMOCHEMISTRY*

Definition.—*Thermochemistry is that branch of the subject of chemistry which treats of the connection between chemical and thermal processes.*

Since almost every chemical reaction is accompanied by an evolution or absorption of heat, and is more or less influenced by changes of temperature, this subject is one of great importance. It must be confessed, however, that the subject is not nearly of the importance it once promised to be, for all recent work has showed that there is no possibility by it of predicting which of two reactions, evolving different amounts of heat will take place. Outside of this possibility there are, however, many other uses to which thermochemistry can be applied, and these we shall study here.

If a substance is changed from one state into another in such a way that all difference in energy appears in one form, as heat, for example, then this amount, when determined, is proportional to the difference of chemical energy in the two states.

Applications of the principle of the conservation of energy.—Hess was the first to apply the principle of the conservation of energy to thermochemistry, although he did not recognize it in that distinct form. In 1840 he found experimentally that *the amount of heat generated by a chemical reaction is the same whether it takes place all at once or in steps.* In other words,

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* For numerical problems illustrating the principles discussed here, see Chapter X

all transformations from the same original state to the same final state liberate the same amount of heat, irrespective of the process by which the final state is reached. The heat liberated in a reaction, then, depends only upon the final and initial states. This was entirely the result of experiment on the part of Hess, who did not consider the principle on which it is based as self-evident, as we do to-day. The truth of this principle he showed by the equality in the heat of formation of ammonium chloride in water when prepared in two dissimilar ways; for he found that

$$\text{gaseous } NH_3 + \text{gaseous } HCl = \text{solid } NH_4Cl + 42100 \text{ cal.},$$

and

$$\text{solid } NH_4Cl + \text{water} = NH_4Cl \text{ in solution} - 3900 \text{ cal.},$$

so that

$$\text{gaseous } NH_3 + \text{gaseous } HCl + \text{water} = NH_4Cl \text{ in solution} + 38200 \text{ cal.};$$

while from

$$\text{gaseous } NH_3 + \text{water} = NH_3 \text{ in solution} + 8400 \text{ cal.}$$

$$\text{gaseous } HCl + \text{water} = HCl \text{ in solution} + 17300 \text{ cal.}$$

and

$$NH_3 \text{ in solution} + HCl \text{ in solution} = NH_4Cl \text{ in solution} + 12300 \text{ cal.}$$

it is evident that

$$\text{gaseous } NH_3 + \text{gaseous } HCl + \text{water} = NH_4Cl \text{ in solution} + 38000 \text{ cal.}$$

Upon this principle of the conservation of energy, applied in this way, the whole subject of thermochemistry is based, for by it it is possible to find indirectly the heat liberated or absorbed by any reaction. *This is true even though it is not possible to carry out the reaction in practice; for then, if it be one which is made up of a number of constituent ones (as the above) all we have to do is to add the constituent reactions and find as a result the heat evolved by the complete reaction. Or, in case a total reaction is known, as well as all its constituent ones but one, subtraction of the sum of the known constituent ones from the main* *one will lead to the heat due to the desired constituent one.* An example of this would be to find the heat of the second reaction above, from the known values of the first and third.

The chemical symbols, as we have used them up to now, have represented only the molecular weights of the substances in question. Now, however, when we are considering as well the quantity of energy absorbed or liberated by the reaction, the symbols have a further meaning which must not be overlooked. In addition to the weight in grams expressed by the formula weights of the substances, the symbols also represent the amount of energy contained in that weight in this state as compared to the energy contained in another, the standard, state. Thus the equation

$$C + 2O = CO_2 + 97000 \text{ cals.}$$

means that the energy contained in 12 grams of solid carbon and 32 grams of gaseous oxygen is greater by 97000 cals. than that contained at the same temperature in 44 grams of gaseous carbon dioxide.

It will be realized from the above that thermochemical equations can be handled exactly as mathematical equations in general, and added to, or subtracted from, one another.

The small calorie, cal., as will be seen, is so small that the numbers employed are very large, and, more important still, do not express well the experimental limitations of the determination. For this reason the Ostwald calorie (Kal.) is much better adapted for the purpose. This is the heat which is necessary to raise the temperature of 1 cc. of H_2O from 0° to 100° C., retaining it in the liquid state, and is related to the so-called large calorie (Cal.) and the small calorie (cal.) in approximately the following way:

$$\text{Kal.} = 100 \text{ cals. (i.e., 1 cc. } H_2O \text{ 1° C.);}$$

$$10 \text{ Kal.} = 1 \text{ Cal. (i.e., 1 kg. of } H_2O \text{ 1° C.).}$$

It will be observed here that one unit in terms of the Ostwald calorie expresses about the limit of accuracy of experimental observations, while of the other two, one leads to the impression that the experimental result is more accurate than it is, the other that it is less accurate.

In addition to these units we also have others which are based upon the erg. The joule, designated by j, is equal to 10^7 ergs, and a unit one thousand times this, i.e., 10^{10} ergs is designated by J. We have, then,

$$1 \text{ cal.} = 4.182 \text{ j and } 1 \text{ j} = 0.2391 \text{ cal.} = 10^7 \text{ ergs},$$

or

$$1 \text{ cal.} = 0.004182 \text{ J and } 1 \text{ J} = 239.1 \text{ cal.} = 10^{10} \text{ ergs}.$$

In all reactions we shall distinguish the state of aggregation by ordinary letters for liquids and solids, and by italics for gases.

In considering substances in solution it is necessary to know the heat which is liberated by this process. This is called the *heat of solution.* For different amounts of water, of course, this will vary, so that for uniformity *the heat of solution is always understood to be the heat* (*positive or negative*) *which is liberated by the solution of 1 mole of substance in so much water that an addition of more water will give no additional heat effect.* This is designated by the addition of the abbreviation Aq (aqua) to the symbol of the substance, and is what was designated as "water" in the equations of Hess above. It is always to be remembered, however, that an isolated Aq in an equation is not equal to an H_2O, which refers to 18 grams of water, although a mole of water may be considered as abstracted from the term Aq, as in the reaction above,

$$NH_3 + \text{Aq} = \text{NH}_4\text{OHAq} + 8400 \text{ cal.},$$

which is considered as if written

$$NH_3 + \text{H}_2\text{O} + \text{Aq} = \text{NH}_4\text{OHAq} + 8400 \text{ cal.}$$

The following example of the determination, by the process of elimination, of the heat liberated by a reaction will probably make the method clear. Calculate the heat evolved by the reaction.

$$MgCl_2+2Na=2NaCl+Mg,$$

when the following experimental data are known:

(−2) $NaCl+Aq=NaClAq-11.8$ Kal.;
(−1) $2H_2+O_2=2H_2O+1368$ Kal.;
(+1) $2Na+O_2+H_2+Aq=2NaOHAq+2236$ Kal.;
(+2) $NaOHAq+HClAq=NaClAq+H_2O+137$ Kal.;
(−1) $Mg+2HClAq=MgCl_2Aq+H_2+1083$ Kal.;
(+1) $MgCl_2+Aq=MgCl_2Aq+359$ Kal.

By adding these equations, after multiplying each of the factors in the parenthesis, we find

$$MgCl_2+2Na=2NaCl+Mg+441.6 \text{ Kal.}$$

In the same way we can find the heat of combustion of carbon in oxygen, a value which cannot be directly measured. Two reactions which have been measured are

$$C+2O=CO_2+970 \text{ Kal.},$$

and

$$CO+O=CO_2+680 \text{ Kal.}(-).$$

Adding these, after changing the signs of the second, we obtain

$$C+O=CO+290 \text{ Kal.},$$

i.e., the sum of energies contained in 12 grams of solid carbon and 16 grams of gaseous oxygen is 290 Kal. greater than that contained in 28 grams of gaseous carbon monoxide.

The process of calculating the heat of a reaction by elimination consists, then, in combining mathematically a number of measured chemical reactions in such a way that the final one is obtained.

The heat of formation.—If the heats of formation of the substances from their elements are known, then it is simpler to substitute these in a reaction and solve for the unknown term. This saves the trouble of eliminating from a large number of equations.

If in a reaction we imagine all substances to be decomposed into their elements before the reaction begins, then the final result of the reaction, after both sides are in the final state, will naturally be the difference in the sums of the heats of formation on the two sides. We have, then, the rule: *To find the heat liberated by a reaction it is simply necessary to subtract the sum of the heats of formation of the original substances from that of those of the final substances, the heat of formation of elements being counted as zero.*

Since, in the reaction,

$$\mathrm{Pb}+2I=\mathrm{PbI_2}+398\ \mathrm{Kal.},$$

$$0=\mathrm{PbI_2}+398\ \mathrm{Kal.},$$

or

$$\mathrm{PbI_2}=-398\ \mathrm{Kal.},$$

we can substitute for the chemical symbols in a thermochemical equation the negative values of the heats of formation, and solve for the unknown term.

Examples.—Find the change in heat energy caused by the decomposition of $\mathrm{MgCl_2}$ by Na. We have

$$\mathrm{MgCl_2}+2\mathrm{Na}=2\mathrm{NaCl}+\mathrm{Mg}+x\ \mathrm{Kal.}$$

The heat of formation of $MgCl_2 = 1510$ Kal. and that of $2NaCl = 1951.6$ Kal., hence

$$-1510 = -1951.6 + x;$$

$$x = 441.6 \text{ Kal.}$$

What is the heat of formation of $KMnO_4$? We have the reaction

$$2KMnO_4Aq + 5SnCl_2 \cdot 16HClAq = 5SnCl_4Aq + 2KClAq$$
$$+ 2MnCl_2Aq + 8H_2O + 3867 \text{ Kal.},$$

or, substituting the negative values of the heats of formation, from the elements of, $5SnCl_2 \cdot 16HClAq$, $5SnCl_4Aq$ and $2KClAq$, respectively, we find

$$-2x - 4057 - 6290 = -7859 - 2023 - 2500 - 5469 + 3867;$$

i.e.,

$$x = 1818 \text{ Kal.},$$

or,

$$K + Mn + 2O_2 = KMnO_4 + 1818 \text{ Kal.},$$

where all are solid but the oxygen.

To obtain this result by the method of simultaneous elimination would require about twenty equations, which in a direct elimination would cause considerable confusion.

This substitution method, when it can be used, is much less confusing than the one based upon one general elimination, for by use of it, at worst, i.e., when the heats of formation have not been directly determined, we can break up the one, general, elimination into as many separate eliminations as there are separate compounds in the reaction. This fact is shown very clearly by a comparison of the two methods as applied to the reaction between solid $MgCl_2$ and solid NaCl. Knowing, in that case, in addition to the six equations given for the elimination, on page 231, that

$$H_2+Cl_2+\mathrm{Aq}=2\mathrm{HClAq}+786 \text{ Kal.},$$

it is possible to break up the one, general, elimination into two separate ones, i.e., one for the heat of formation of solid $MgCl_2$, the other for solid NaCl. These two values can then be substituted in the original equation, just as though they had been found directly and the result obtained without the possibility of confusion which might otherwise be present. In fact this was done above.

The heat of formation of organic compounds can be found from the heats of combustion in oxygen. If the elements remain behind in the uncombined state the negative value of the heat of combustion would be the heat of formation. The elements, however, unite to form H_2O, CO_2, etc., so that the heats of formation of these must be subtracted from the heat measured to obtain the true value of the heat of formation from the elements.

In order to save time, heats of formation, instead of being given in full, as

$$H_2+Cl_2+\mathrm{Aq}=2\mathrm{HClAq}+786 \text{ Kal.},$$

are often written in the form

$$(H_2,\ Cl_2,\ \mathrm{Aq})=786 \text{ Kal.};$$

i.e., only the substances on the left of the chemical equation are given, and are separated by commas and inclosed in a parenthesis.

Chemical changes at a constant volume.—When the volume of a chemical reaction is held constant, or *when the external work (positive or negative) involved in the change in volume is not* *included in the heat of the reaction*, the reaction is said to take place *at constant volume.* In other words, the condition of constant volume means the condition involving no positive or negative external work to the system. Under such conditions *the energy in one state is then simply equal to that in the other, plus the amount of heat generated by the change.* The chemical symbols which we use in such cases express, in addition to the ordinary chemical meaning, *the energy contained in one mole.*

Chemical changes at a constant pressure.—If the volume changes during the reaction, and the system loses heat equivalent to the work of expansion, or gains heat equivalent to the work done upon it by a compression, the reaction is said to take place at *constant pressure.* The only difference between constant volume and constant pressure conditions, then, is that no matter how the volume may change, the heat equivalent to the work of the change is not considered as affecting the energy of the system under constant volume conditions, while it is considered as a loss (expansion) or a gain (compression) to the system when under constant pressure conditions.

This loss or gain may be neglected in all cases where no gas is formed, simply because the correction is very small as compared to the heat of the reaction. Thus, for example, we will calculate the correction to be used for an increase of volume equal to 1 cc. Here $\Delta v = 1$ and $p = 1033.6$ grams and the work, $p\Delta v = 1033.6$ gr.-cms., which is equal to

$$\frac{1033.6}{42600} = 0.02426 + \text{cal. or } 0.00024 \text{ Kal.}$$

If 1 mole of base is mixed with 1 mole of acid 137 Kal. are generated, and the volume increase is equal to 20 cc. Hence the correction to be applied here is

$$20 \times 0.000243 \text{ Kal.} = 0.00486 \text{ Kal.},$$

which is so small compared to 137 Kal. that it may be neglected.

When a gas is formed, however, the increase of volume may become very large; consequently it is necessary in such cases to use the correction. By definition the external work done by the formation at T° of 1 mole of gas from negligible volume, against any constant pressure, is $2T$ cal., or $0.02T$ Kal., and for N moles is $0.02NT$ Kal., hence, *in any reaction, for each mole of gas formed, at the absolute temperature* T, *under constant pressure conditions, the energy of the substance is decreased by* $0.02T$ *Kal.*

In the case of the absorption of the gas, on the other hand, the energy is increased by this amount.

Thus if 1 mole of gas is formed by a reaction against any constant pressure, at 18° C., the amount of heat used for its formation is

$$0.02\times(273^\circ+18)=5.82 \text{ Kal.}$$

And at any one temperature this is independent of the pressure p, so long as this remains constant.

Under constant pressure, the symbols, in addition to the chemical significance, represent the energy *plus the term* pv *for 1 mole.* This term pv_m may be either positive or negative, according as the gas is absorbed or formed.

Relation between results for constant volume and constant pressure.—Since what we call the constant volume condition is a no-external-work condition, whether the volume really remains constant or not, and a constant-pressure condition is an external-work condition, no matter how the pressure varies so long as the volume changes; and external work done means a loss of heat, and work done upon the system means a gain of heat, it is evident that the relation between the heat energy of a reaction at constant volume and that at constant pressure against any constant can be represented by the equation

$$Q_p=Q_v-N(0.02T \text{ Kal.}),$$

where N is the number of moles of gas *formed* (=final moles − original moles) in excess of those originally present, and consequently is negative when gas, in place of being formed, is absorbed by the reaction. In general it is simpler to reason out which is the larger, Q_v or Q_p, than to use the equation. In all cases where the reaction goes with an increase of moles (volume) the heat at constant pressure must be less than that at constant volume, for some of the heat has been used to do the external work of expansion. If the number of moles (the volume) decreases, then Q_p will be larger than Q_v, for external work has been done on the system, and heat equivalent to it absorbed.

In this way it is possible to make all our determinations for constant volume and then calculate the result to constant pressure. This latter is the more useful term, for all our reactions take place in that way under atmospheric pressure. The former, however, is that usually determined in the bomb-calorimeter. An example of the calculation from one condition to the other is given below. Find from the reaction

$$H_2+O=\mathrm{H_2O}+674.84 \text{ Kal. at } 18^\circ \text{ const. vol.},$$

the heat generated if the reaction forming liquid water from the gases, hydrogen and oxygen takes place under a constant pressure. By the reaction 1 mole of hydrogen disappears with 1/2 of a mole of oxygen and forms 1 mole of liquid water (no gas); consequently the heat under constant pressure will be larger than that for constant volume by the amount $1\frac{1}{2}\times 0.02T$ Kal., for $N=-1\frac{1}{2}$, i.e., $1\frac{1}{2}$ moles are lost by the reaction. We have, then,

$$674.84+1\tfrac{1}{2}\times 0.02\times 291=683.57 \text{ Kal.}=Q_p,$$

as the value for constant pressure at 18° C.

Effect of temperature.—If we allow a reaction to take place first at the temperature T and then at the temperature $T+\Delta T$, the amounts of heat evolved are found to be different; assume them to be Q_1 and Q_2 respectively.

Starting with the constituents, imagine the reaction taking place at the temperature T, at which the amount of heat Q_1 is evolved, and then heated to the temperature $T+\Delta T$. If s' is the *total heat capacity of the resulting products* the amount of heat necessary for this rise in temperature is $s'(\Delta T)$. The reaction has now taken place and the temperature is $T+\Delta T$.

Starting again with the constituents at the temperature T assume them to be heated to $T+\Delta T$ and then to react, evolving the heat Q_2. The heat necessary for this rise in temperature is $s(\Delta T)$, *where s is the total heat capacity of the original substances.*

We have started, thus, with the same original substances, at the same temperature, and obtained the same products, at the same final temperature; hence, by the law of the conservation of energy (pp. 49–52) the amounts of heat involved must be the same. We have, then,

$$Q_1-s'(\Delta T)=Q_2-s(\Delta T),$$

i.e.,

$$Q_2-Q_1=(s-s')(\Delta T),$$

$$\frac{Q_2-Q_1}{\Delta T}=s_{\text{orig.}}-s_{\text{final}},$$

or,

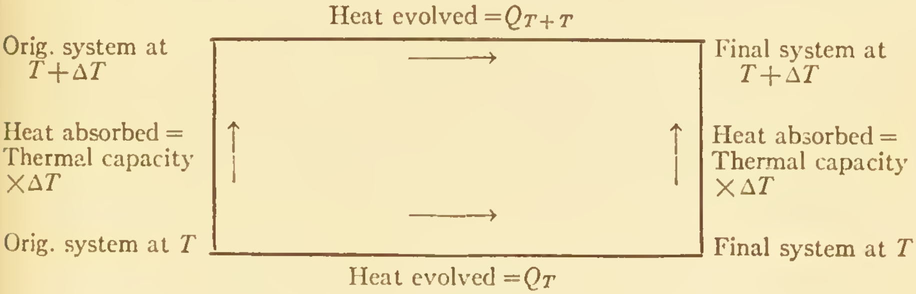
$$\frac{\Delta Q}{\Delta T}=s_{\text{orig.}}-s_{\text{final}}.$$

The change in the heat of reaction per degree of temperature is equal to the amount of heat necessary to raise the temperature of the total weight of the left side of the chemical equation 1°, minus that necessary to raise the total weight of the right side 1°.

It will be observed, then, that the only change in the heat of reaction with the temperature is that due to the specific heat of the substances present.

The term $(s_{\text{orig.}} - s_{\text{final}})$, here, is found by first getting the various products of the number of moles of each constituent, into its molecular weight, into its specific heat, and then subtracting the sum of those representing the final state of the system from that of those representing the original state. Naturally, if the heat Q refers to constant pressure, and the system includes gases, the specific heat for the gases must be those at constant pressure, Q_p; and for the variation of Q_v with the temperature the specific heats at constant volume would be employed.

The derivation of this relation can also be illustrated by a diagram similar to the one employed in the discussion of liquids on page 93.


Heat evolved $= Q_{T+T}$
Orig. system at $T+\Delta T$
Final system at $T+\Delta T$
Heat absorbed = Thermal capacity $\times \Delta T$
Heat absorbed = Thermal capacity $\times \Delta T$
Orig. system at T
Final system at T
Heat evolved $= Q_T$

It is to be noted here that if s_{final} is larger than $s_{\text{orig.}}$ the sign of $\frac{\Delta Q}{\Delta T}$ will be negative. This indicates that an increase of temperature causes a decrease in the heat of the reaction, i.e., the heat varies inversely with the temperature. If s_{final} is smaller than $s_{\text{orig.}}$ the term $\frac{\Delta Q}{\Delta T}$ is positive and Q varies directly as the temperature.

Example.—When 4 grams of hydrogen at 18° combine with 32 grams of oxygen at the same temperature to produce 36 grams of liquid water, 1367.1 Kal. are evolved. How much heat will be evolved if the same masses of hydrogen and oxygen combine at the temperature of 200° and the product of the combination is maintained at this temperature, the pressure being constant? The specific heats per gram are: 3.409 for H, 0.2175 for O, 1 for H_2O from 18° to 100°, and 0.4805 for H_2O between 100° to 200°. The latent heat of evaporation of water is 536.5, all values being expressed in small calories.

For liquid water up to 100° we have the relation

$$(4\times3.409+32\times0.2175)-(36\times1)=\frac{\Delta Q}{\Delta T}=-15.404 \text{ cals.},$$

and since this is for 1°, we have for the 82° (i.e., for $100-18$), $82\times(-15.404)=1263$ cals. The heat of formation of liquid water at 100°, from the mixture of gases at 100°, then, is

$$1367.1-12.63=1354.47 \text{ Kal.}$$

But in going into water-vapor at 100°, 36×536.5 cals. of this, by external as well as internal work, is absorbed by the system, i.e., hydrogen and oxygen forming gaseous water at 100° evolve

$$1354.47-193.14=1161.33 \text{ Kal.}$$

For the reaction between 100° and 200° for gaseous water, as formed from gaseous hydrogen and oxygen, we have the temperature coefficient

$$(4\times3.409+32\times0.2175)-36\times0.4805)=\frac{\Delta Q}{\Delta T}=2.3 \text{ cals.},$$

and, for the interval of 100°, (i.e., for $200-100$),

$$100\times2.3=230 \text{ cals.}=2.3 \text{ Kal.}$$

In total, then, we have

$$1161.33+2.3=1163.63 \text{ Kal.}$$

as the heat of transformation according to the reaction

$$2H_2+O_2=H_2O, \text{ all at } 200° \text{ C.}$$

It is also possible, naturally, to find qualitatively how a change in temperature will affect a reaction, by the aid of the theorem of Le Chatelier. *When a reaction evolves heat, for example, it is quite evident that an increase of temperature will cause it to go in the opposite direction—while when it absorbs heat, high temperature will cause it to go further in that direction.*

The thermal reactions of electrolytes.—*Two salt solutions which are so dilute that the ratio* $\frac{\Lambda_{vc}}{\Lambda_\infty}$ (p. 206) *is equal to* 1, *do not evolve or absorb heat when mixed, provided no chemical reaction takes place between them.*

This fact was first observed by Hess and has been confirmed by all observers since.

Another experimental fact observed to hold for solutions of electrolytes is as follows: *When an acid is neutralized by a base, both being in so great a dilution that the value* $\frac{\Lambda_{vc}}{\Lambda_\infty}$ *for each is equal to* 1, *and this condition is also fulfilled for the salt formed, the heat evolved is equal to 137 Kal. per mole of water formed, and is independent of the nature of the base and acid used, and the salt formed, so long as this latter at that dilution fulfills the condition* $\frac{\Lambda_{vc}}{\Lambda_\infty}=1$.

These facts, taken in connection with those mentioned above (pp. 201–208) and the conclusions arrived at there, are not so startling as one might imagine at first glance. Since for the acid and base we have the relation

$$\Lambda_{\infty \text{acid}} + \Lambda_{\infty \text{base}} - \text{const.} = \Lambda_{\infty \text{salt}},$$

the *constant being independent of the nature of either the acid, the base, or the salt*, and, since the salt is observed to have a molecular weight (by definition) equal to one-half the formula weight, i.e., is completely ionized according to all the possible methods of measurement, it is quite certain that the system is made up of the substances previously composing the acid and base in the same state as that in which they existed in them. In other words, expressing the chemical equation in accord with the experimental facts above, we have

$$H^+ + A^- + M^+ + OH^- + NH_2O = A^- + M^+ + (N+1)H_2O,$$

where N represents the number of moles of water present in the system before the reaction.

Since the conductivity shows the constituents of the salt (the ions) to be present in the same form they were in originally, the *only portion of the reaction which could possibly involve heat is the formation of water from the ionized hydrogen* (H^+) *and the ionized hydroxyl* (OH^-). As we know that hydrogen and hydroxyl in the ionized state can exist together to but an infinitesimal extent (for pure water conducts only very slightly), the following conclusion is certainly justified. When an acid unites with a base (at any rate in the condition in which we have assumed them) the cause of the reaction is the inability of ionized hydrogen to exist in the presence of ionized hydroxyl beyond an exceedingly small amount; and the heat of the neutralization (for this case) is that heat which is evolved by the formation of *water from its ions* in this way, i.e., 137 Kal. for each mole of H^+ and OH^- (by definition) forming one mole of H_2O at 25°.

By a method which we shall consider later (Chapter VIII) it is possible not only to show the presence of, but to calculate accurately, the heat involved by the ionization of a substance. When the acid and salt are completely ionized, for example, and the base but slightly, it is possible to show just how much extra heat (either positive or negative) is involved by the further ionization of the base. For the partly dissociated base must increase in dissociation as its ionized OH is used up, since the more dilute the solution of the base the greater must be its ionization, up to a certain point.

If both the acid and base are but partly ionized the result will differ still more, for heat will be absorbed or evolved by the further dissociation of both of these. And if the salt formed is not completely ionized, i.e., if more heat is liberated or absorbed by its undissociated product being formed, we shall also have a still further quantity to account for.

It is evident, then, that *the heat generated by the neutralization of an acid by a base is equal, for each mole of water formed, to 137 Kal., plus the heat produced by the amount of un-ionized salt formed, plus the sum of the heats evolved in the completion of the ionizations of the acid and the base.* For, in general, heat is evolved by the process of ionization, and, consequently, absorbed when un-ionized substance is formed.

It is for this reason that we get a larger heat of neutralization for certain acids with caustic soda than for others, for heat is given out by the further ionization of the acid (though an amount is always absorbed by the opposite process, i.e., association of the salt, if that takes place) *and consequently the heat of neutralization is in no sense a criterion as to the strength of the acid.*

Later we shall consider this relation more in detail, i.e., after we have studied the method to be used for the calculation of the heat of dissociation.

It is obvious from the above that the thermal properties of electrolytes are additive when they are in such a dilution that they fulfill the condition $\frac{\Lambda_{vc}}{\Lambda_\infty}=1$. When not in this condition the change in the thermal effect depends upon the amount of heat involved in causing them to alter their states.

When a precipitate is formed in such a solution (i.e., when a chemical reaction takes place, which was excluded above) it is often possible to find its heat of formation just as we found that of water. An example of this is the following:

$$\mathrm{Ag^+Aq+NO_3^-Aq+Na^+Aq+Cl^-Aq=AgClAq+}$$
$$\mathrm{Na^+Aq+NO_3^-Aq+158\ Kal.}$$

or

$$\mathrm{Ag^+Aq+Cl^-Aq=AgClAq+158\ Kal.}$$

i.e., when 1 mole of AgCl is formed, from the ionized silver and ionized chlorine in a solution, heat equal to 158 Kal. is evolved. Conversely if 1 mole of AgCl were dissolved, this amount of heat would be absorbed, i.e., the heat of solution of a substance into its ions is equal to the negative value of the heat of precipitation from its ions.

Although the above method is not always possible, we can find the heat of formation in solution in another way. The principle of this is as follows: By electrical measurements it has been possible to find the amount of heat involved when 2 grams of gaseous hydrogen form 2 grams of ionized hydrogen in solution. This value is approximately equal to 4 J, but since there is some uncertainty about its exact value, it is usual to assume it equal to zero. Later, then, the results based upon this can be readily recalculated. By dissolving a metal in a completely ionized acid, then, i.e., by the substitution of metal in the ionized state for the hydrogen, which is evolved as a gas from that state, we observe directly the heat of formation of the ionized metal from massive metal. By then observing the heat of solution of a completely ionized salt of this metal, the heat due to the negative radical can also be determined, for the heat of solution of the salt is equal to the sum of the heats of ionization of the constituents.

In this way the table below has been prepared by Ostwald. In order to find the heat of formation of the salt it is only necessary to form the sum of the heats due to the ions into which it decomposes, taking into account the valence of the ions as indicated by the + signs for the electro-positive and the − signs for the electro-negative substances.

Cations.		J = joules × 10³.
Hydrogen	H^+	+ 0
Potassium	K^+	+259
Sodium	Na^+	+240
Lithium	Li^+	+263
Rubidium	Rb^+	+262
Ammonium	NH_4^+	+137
Hydroxylamine	NH_4O^+	+157
Magnesium	Mg^{++}	+456
Calcium	Ca^{++}	+458(?)
Strontium	Sr^{++}	+501
Aluminium	Al^{+++}	+506
Manganese	Mn^{++}	+210
Iron	Fe^{++}	+ 93
	Fe^{+++}	− 39
Cobalt	CO^{++}	+ 71
Nickel	Ni^{++}	+ 67
Zinc	Zn^{++}	+147
Cadmium	Cd^{++}	+ 77
Copper	Cu^{++}	− 66
	Cu^+	−67(?)
Mercury	Hg^+	− 85
Silver	Ag^+	−106
Thallium	Tl^+	+ 7
Lead	Pb^{++}	+ 2
Tin	Sn^{+++}	+ 14

Anions of		J = joules × 10³.
Hydrochloric acid	Cl^-	+ 164
Hypochlorous acid	ClO^-	+ 109
Chloric acid	ClO_3^-	+ 98
Perchloric acid	ClO_4^-	− 162
Hydrobromic	Br^-	+ 118
Bromic acid	BrO_3^-	+ 47
Hydriodic acid	I^-	+ 55
Iodic acid	IO_3^-	+ 234
Periodic acid	IO_4^-	+ 195
Hydrosulphuric acid	S^{--}	− 53
	HS^-	+ 5
Thiosulphuric acid	$S_2O_3^{--}$	+ 581
Dithionic acid	$S_2O_6^{--}$	+1166
Tetrathionic acid	$S_4O_6^{--}$	+1093
Sulphurous acid	SO_3^{--}	+ 633
Sulphuric acid	SO_4^{--}	+ 897
Hydrogen selenide	Se^{--}	− 149
Selenious acid	SeO_3^{--}	+ 501
Selenic acid	SeO_4^{--}	+ 607
Hydrogen telluride	Te^{--}	− 146
Tellurous acid	TeO_3^{--}	+ 323
Telluric acid	TeO_4^{--}	+ 412
Nitrous acid	NO_2^-	+ 113
Nitric acid	NO_3^-	+ 205
Phosphorous acid	HPO_3^-	+ 603
Phosphoric acid	PO_4^{---}	+1246
	HPO_4^{--}	+1277
Arsenic acid	AsO_4^{---}	+ 900
Hydroxyl	OH^-	+ 228
Carbonic acid	HCO_3^-	+ 683
	CO_3^{--}	+ 674

These numbers hold only for the case that the substances are in very dilute solution, i.e., Aq should be added to the symbol of each ion. For stronger solutions, in which the ionization is not complete, other amounts of heat are involved which, unless allowed for, will lead to incorrect results.

The equations

$$\mathrm{Na} = \mathrm{Na}^{+} + 240\ \mathrm{J}$$

and

$$\mathrm{Cl}_2 = 2\mathrm{Cl}^{-} + 2 \times 164\ \mathrm{J},$$

for example, mean that by the transformation of the formula weight of metallic sodium into the ionized state 240 J are evolved; and by the change of the formula weight of chlorine gas into two formula weights of ionized chlorine (p. 207) 2×164 J are liberated.

CHAPTER VIII

CHEMICAL CHANGE *

A. EQUILIBRIUM AND THE CRITERION OF EQUILIBRIUM

Reversible reactions.—If we bring a number of reacting substances together in a chemical system, and leave them for a sufficient length of time, the reaction will reach an end, and we shall have, according to a previous general definition, a solution, i.e., a mixture containing solids, gases, or liquids, or all three.

To represent any chemical reaction we may use the equation

$$N_1A_1+N_2A_2+N_3A_3+\ \ldots\ =N_1'A_1'+N_2'A_2'+N_3'A_3'+\ \ldots,$$

where N_1 moles of A_1, N_2 of A_2, N_3 of A_3, etc., unite to form N_1' moles of A_1', N_2' of A_2', N_3' of A_3', etc. When an amount of each of these substances can remain together for an indefinite length of time, without the reaction going in either direction to produce a lasting change, they are said to exist in chemical equilibrium.

Reactions which go partly from left to right when we start with the substances A_1, A_2, etc., and partly from right to left when we start with A_1', A_2', etc., are called *reversible or reciprocal reactions, provided that in each case, starting with equivalent amounts, the final equilibrium is the same from both directions;*

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* For numerical problems illustrating the principles discussed in this chapter, see Chapter X.

or, in other words, *the equilibrium state is the common limit of two inverse reactions.*

An excellent example of such a reaction is

$$\underset{\text{Alcohol.}}{C_2H_5OH}+\underset{\text{Acetic Acid.}}{CH_3COOH} \rightleftarrows \underset{\text{Ethyl Acetate.}}{CH_3COOC_2H_5}+\underset{\text{Water.}}{H_2O}.$$

If we start with the substances on the left side we obtain a certain definite amount of those on right and *vice versa*, independent, *in this particular case*, of the temperature. For example, 1 mole (46 grams) of alcohol plus 1 mole (60 grams) of acetic acid, or 1 mole (88 grams) of ethyl acetate plus 1 mole (18 grams) of water, will always give the same final state, in which we have

$$1/3 \text{ mole alcohol} + 1/3 \text{ mole acetate acid} \\ + 2/3 \text{ mole ethyl acetate} + 2/3 \text{ mole water.}$$

While the above is true for many chemical reactions, it is by no means true for all, for many reactions are *practically* complete, i.e., limited in extent only by the amounts of the reacting constituents present, the reaction progressing until one of the constituents has practically disappeared entirely. This is the case when hydrogen and chlorine unite to form hydrochloric acid gas, or when hydrogen and oxygen form water, both at low temperatures. In each case one at least of the constituents practically disappears entirely. At higher temperatures, however, both of these systems lead to an equilibrium state, in which all the gases exist permanently in considerable amounts which are dependent upon the pressure and temperature, but which is independent of the direction from which the equilibrium was produced. Thus, even in the hottest part of the oxy-hydrogen flame we find uncombined hydrogen and oxygen, as well as the product of the reaction, water vapor. And, if water is heated to this temperature, we obtain an equilibrium which is identical with this, as far as concerns the proportions of the three substances. The higher the temperature, here, the greater will be the proportions of the uncombined gases, i.e., the greater will be the dissociation of water vapor (see Table, p. 36).

This establishment of an identical equilibrium from both directions is the best experimental test we have of a *true* equilibrium. Owing to the fact that the speed of a reaction, of itself, toward the equilibrium state may be almost infinitesimal, we are often confronted with states of *apparent* or *false* equilibrium, which is not *true* equilibrium, for the reaction in many cases, over very long periods of time, can be shown to be really progressing, though at a speed which makes its measurement over shorter periods impossible. Thus, at low temperatures, hydrogen and oxygen gases *appear* to be in equilibrium when mixed, without uniting to form water; and but a small change can be noticed in their state even after years of standing. If, however, we pass an electric spark through the mixture, or expose to it a piece of spongy platinum, reaction takes place completely and instantaneously, and practically we have only pure water and water vapor present, unless one of the original gases was present in excess over the other, when that excess will also remain uncombined. This naturally shows that our apparent equilibrium between the constituents only, was a false equilibrium—which is also shown, of course, by the fact that that same state would not be obtained spontaneously from the water side of the reaction at that temperature. Montier (Bull. Soc. philomathique, (7), 4, 86, 1880) has summed up the experimental versus the thermodynamical aspects here, somewhat as follows: Whenever thermodynamics predicts that a certain equilibrium state of a given system should exist, experiment confirms it; but when thermodynamics states that a system will undergo a certain transformation, it may happen, after the system has been placed in that state, that experimentally it will be found to be in *apparent* equilibrium.

Naturally, the difference here lies in the fact that thermodynamics does not consider at all the time element, in connection with chemical equilibrium; while that is a very essential thing, experimentally. In the following pages we shall consider only the state of *true* equilibrium, and shall always make sure, in any given case, that the reaction is in that condition, both by the experimental test of finding an identical state from both sides of the reaction, as well as by the thermodynamical one. Here we are aided very materially from the experimental point of view, by the existence of catalysers or catalysts, which change the speed of the reaction, without either entering into it themselves, or in any way altering the proportions of the products produced in the final equilibrium. In the above illustrative case both the electric spark and the spongy platinum were catalysts with respect to the reaction $H_2+\frac{1}{2}O_2 \rightarrow H_2O$.

The law of mass action. The criterion of equilibrium.—Considering such a reversible reaction as that above, or, for example,

$$2HI \rightleftarrows H_2+I_2,$$

the question at once arises—in which direction and to what extent will such a reaction go when we start, for instance, with a certain concentration or pressure of each of the three gaseous constituents, HI, I and H?

From the purely chemical point of view the above equation simply provides that *if* we start with 1 mole of hydrogen and 1 mole of iodine, and *if* these unite completely, 2 moles of hydriodic acid gas will be formed; or *if* we start with 2 moles of hydriodic acid gas, and this is completely decomposed, we shall obtain 1 mole each of hydrogen and iodine; or *if* we start with 1 mole of hydrogen and 1 mole of iodine, and lose x moles of each, $2x$ moles of hydriodic acid gas will be formed; or starting with 1 mole of hydriodic acid and losing y moles, $\frac{1}{2}y$ moles of each, hydrogen and iodine, will be formed. As to *what* portion of the hydrogen and iodine will unite to form hydriodic acid; or *what* portion of a total original amount of hydriodic acid will decompose to form hydrogen and iodine; or what will take place if all three are mixed together; we are utterly ignorant, failing further information than that contained in the chemical equation.

The answers to these questions can only be obtained by the application of a very general law which was first found experimentally by Guldberg and Waage in 1864. The *qualitative* form of this *law of mass action* is as follows: *Chemical action, at any stage of the process, is proportional to the active masses of the substances present at that time, i.e., to the amounts of each present in the unit of volume.*

In this form, however, the law of mass action is of but little practical use. It will be necessary, then, for us to derive a quantitative expression of it, and thus to obtain it in such a form that it may be applied to our needs in answering questions such as those alluded to above. It is evident here that by the finding of a *criterion of equilibrium*, expressed in terms of the partial pressures or concentrations of the various substances present in the equilibrium, all questions such as those above could be readily answered. And we find in fact that the *mathematical, quantitative*, expression of this law of mass action is simply such a criterion of equilibrium, i.e., a statement of the relative amount of each substance which can exist in the *final* equilibrium; so that knowing the *original* amounts we start with, we have no difficulty by its aid in calculating the amount of the change necessary to carry the system from that original state to the equilibrium state.

Imagine a reaction of the type

$$N_1A_1+N_2A_2 \rightleftarrows N_1'A_1'+N_2'A_2',$$

where all the substances are gaseous, having taken place in a closed vessel and to have attained a state of equilibrium in which the partial pressures of the constituents are equal respectively to p_1, p_2, p_1' and p_2'.

Assume, further, that it is possible to insert each of the substances on the left against its gaseous pressure p_1, p_2, and to remove each of the products, as they are formed, from the gaseous pressure p_1', p_2', to the original external pressure p_0—and that this insertion and removal is isothermal and reversible. This insertion and removal of substance may be imagined as taking place through the agency of as many semi-permeable partitions as there are substances in the system, where the counter pressure, for example, resisting the insertion of any one substance into the system through its partition, will be only the pressure of that substance itself which is then present in the system; for that partition is permeable only to that substance.

For the description of a device of such a nature, and for the rigid derivation of this and other laws by aid of the device, see Washburn (J. Am. Chem. Soc., 32, 467–502, 1910).

Since by such a series of operations we would do work on one side (−), and obtain work (+) from the other, the sum of the two amounts (regarding the signs) would give us an expression for the work (+ or −) which is done *by the system itself* during the transformation, at constant temperature, of N_1 moles of A_1 and N_2 moles of A_2 to N_1' moles of A_1' and N_2' moles of A_2', the initial and final pressure being the same, viz., p_0. And this in its turn would lead to the expression of the quantitative relation existing between the constituents at equilibrium, i.e., to the *criterion of equilibrium* we seek.

Since the work required to change the pressure of 1 mole of gas from p_0 to p_1, or to insert 1 mole of the gas from the pressure p_0 into a space in which that substance has the constant pressure p_1, is given by the expression $RT \log_e \frac{p_1}{p_0}$,* the work of insertion of the N_1 moles of the substance A, will be $N_1RT \log_e \frac{p_1}{p_0}$, or $RT \log_e \frac{p_1^{N_1}}{p_0^{N_1}}$. For the work of insertion of the N_2 moles of A_2 from the external pressure p_0 against the constant, internal pressure of A_2, viz., p_2, we have the corresponding expression $N_2RT \log_e \frac{p_2}{p_0}$, or $RT \log_e \frac{p_2^{N_2}}{p_0^{N_2}}$. The sum of these two terms, then, with a negative sign, is equal to the amount of work gained by us during the process, i.e.,

$$-RT \log_e \frac{p_1^{N_1} p_2^{N_2}}{p_0^{N_1} p_0^{N_2}}.$$

By the removal as they are formed (thus leaving the intermediate chemical system always in equilibrium) of N_1' moles of A_1', at the pressure p_1', and of N_2' moles of A_2', at the pressure p_2', to the original pressure p_0, the amount of work (a gain to us, and positive in sign, for it is in the opposite direction, and hence must have a different sign from the one above) is naturally equal to the sum of $RT \log_e \frac{p_1'^{N_1'}}{p_0^{N_1'}}$, and $RT \log_e \frac{p_2'^{N_2'}}{p_0^{N_2'}}$, i.e., to

$$RT \log_e \frac{p_1'^{N_1'} p_2'^{N_2'}}{p_0^{N_1'} p_0^{N_2'}}.$$

In total, then, the gain of work by us (i.e., *the work* PERFORMED *by the system in* transforming N_1 moles of A_1 and N_2 moles of A_2, both at the pressure p_0, into N_1' moles of A_1' and N_2'

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* Work$=v_m dp=\frac{RT}{p}dp=RT\int_{p_0}^{p_1}\frac{dp}{p}=RT \log_e \frac{p_1}{p_0}$.

moles of A_2', also at the pressure p_0, at the constant temperature T, the intermediate chemical system by aid of which the transformation is made always remaining in equilibrium, is equal to the sum of these two expressions; which becomes, when rearranged

$$W = RT \log_e \frac{p_1'^{N'} p_2'^{N_2'}}{p_1^{N_1} p_2^{N_2}} - RT \log_e \frac{p_0^{N_1'} p_0^{N_2'}}{p_0^{N_1} p_0^{N_2}}. \quad . \quad . \quad (18)$$

The sign of W, here, i.e., the indication as to whether a system really gains or loses energy during the reaction will depend upon the relation in value of the numerators and denominators of the fractions; when the denominators are the larger, the logarithm to the base e will naturally be negative, and when W has a negative sign, work will have to be performed upon the system to cause the change to take place.

As the processes of insertion and removal are assumed here, to be isothermal and reversible, this amount of work, W, must be *the maximum work which can be performed by this system under these conditions; and consequently it must be constant in value at any one constant temperature,* so long as the pressures from which the original substances are added, and to which the final substances are removed, is p_0.*

It is evident here, however, that the maximum work performed by the entire system must be independent of the pro-

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* Naturally, the same form of equation would be obtained here if we had started with the constituents at the different pressure p_{A_1}, and p_{A_2}, instead of having both at p_0; and had carried the final products to the still different pressures p_{A_1}'; and p_{A_2}' instead of to the common value p_0. The second term of (18) under these conditions would then become $-RT \log_e \frac{p_{A'_1}^{N'_1} p_{A'_2}^{N_2'}}{p_{A_1}^{N_1} p_{A_2}^{N_2}}$.

Equation (18) is also sometimes written so that the second term is

$$+RT \log_e \frac{p_0^{N_1} p_0^{N_2}}{p_0^{N_1'} p_0^{N_2'}},$$

i.e., is the reciprocal form of the above and so has the contrary sign.

portions of the substances in the reacting mixture itself (the first term of the equation), since that acts only as an intermediary, which suffers no appreciable change during the process; for it was in equilibrium before the addition of the substances, and is left in equilibrium after the removal of the products formed by it. The maximum work, *at that same temperature,* then, when p_0 has the different value p, would differ from the above only by reason of the corresponding changes produced in the value of the second term of the equation. Hence, *at any one temperature, the first term must remain constant for any one reaction,* and we have

$$\text{constant} = RT \log_e \frac{p_1'^{N_1'} p_2'^{N_2'}}{p_1^{N_1} p_2^{N_2}};$$

and since, if the logarithm to the base e of an expression is constant, the expression itself must be constant, and since R is also a constant, we have *at any one constant temperature,* T,

$$\text{constant} = K_p = \frac{p_1'^{N_1} p_2'^{N_2'}}{p_1^{N_1} p_2^{N_2}}, \quad . \quad . \quad . \quad . \quad (19)$$

where the constant K_p includes all the other constants.

Further, since, *at any one constant temperature,* T, pressures and concentrations are proportional, we must also have,

$$K_c = \frac{c_1'^{N_1'} c_2'^{N_2'}}{c_1^{N_1} c_2^{N_2}}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (20)$$

where the relationship between K_p and K_c, since $c = \frac{1}{v_m} = \frac{p}{RT}$, is

$$K_c = \frac{p_1'^{N_1'}\left(\frac{1}{RT}\right)^{N_1'} \cdot p_2'^{N_2'}\left(\frac{1}{RT}\right)^{N_2'}}{p_1^{N_1}\left(\frac{1}{RT}\right)^{N_1} \cdot p_2^{N_2}\left(\frac{1}{RT}\right)^{N_2}} = K_p(RT)^{N_1+N_2-N_1'-N_2'};$$

which, designating the summation of the original moles by ΣN, and that of the final ones by $\Sigma N'$, becomes

$$K_c = K_p(RT)^{\Sigma N - \Sigma N'}. \quad . \quad . \quad . \quad . \quad . \quad (21)$$

The constant for concentrations is equal to that for pressures, multiplied by RT raised to a power equal to the difference between the number of moles originally present and those finally present, according to the chemical equation. This value $\Sigma N - \Sigma N'$ is always constant for the same chemical reaction, independent of the moles of substance that may be present in the specific case studied; for it is simply *the difference between the summation of the coefficients* (*i.e., numbers of molecular weights*) *on the two sides of the correctly written chemical equation, i.e., where the chemical symbols themselves represent molecular weights.* In case $\Sigma N - \Sigma N' = 0$, i.e., where we have the same number of moles on both sides ($H_2 + I_2 = 2HI$), it is apparent that $K_c = K_p$; and that any other quantity, proportional to the number of moles present, volumes in cubic centimeters, for example, could be used in place of the c's or p's, without changing their identical value of K; for any factor used in both numerator and denominator, would cancel in finding the value of K.

The constant K, either in the form obtained for pressures, K_p, or that for concentrations, K_c, is known as *the constant of equilibrium*, or *the constant of the law of Mass Action*, and is *the criterion of equilibrium of a chemical reaction*, which we have sought.

In words, we may express equations (19) and (20), the *criteria of chemical equilibrium*, as follows: *According to the law of mass action*, AT EQUILIBRIUM AND AT ANY ONE CONSTANT TEMPERATURE, *for any one reversible chemical reaction, the product of the pressures* (*concentrations*) *of the substances on the right* (*the final ones*), *each raised to a power equal to the number of moles reacting* (*according to the chemical reaction*), *divided by the prod-*

uct of the pressures (concentrations) of the substances on the left (initial ones), each raised to a corresponding power, is a constant.

Since in deriving these criteria of equilibrium we have assumed the gas laws, as expressed by $pv_m = RT$, to hold, *the law of mass action in this form will only hold rigidly for those cases where the product of pressure and volume, for the constituents of the reaction, is a constant.* The placing of the substances on the right of the reaction always in the numerator of the fraction giving the value of K is conventional; but it must be remembered that the reciprocal form would also remain constant, though it would undoubtedly lead to confusion if used at present.

The change of free energy in a chemical reaction.—The *decrease of free energy* of a given isothermal process (i.e., $-\Delta F$) is defined by Lewis (Zeit. f. phys. Chem., 26, 161, 1907) as the maximum work which the process can *perform*, exclusive of the work against the external pressure. The negative value of this decrease in free energy is then *the increase in free energy*, i.e., ΔF. The change in free energy in a system, thus represents the work producible by the system, and which is actually available for any desired purpose; and is dependent solely upon the initial and final states of the system.

The importance of this concept of the change in free energy during a reaction, in the study of chemical phenomena, can best be realized from the following facts brought out by Lewis. *At equilibrium the change in free energy in a system is equal to zero, i.e.,* $\Delta F = 0$; i.e., it is only when the free energy of the original substances is equal to that of the final substances, that equilibrium is possible between them. This, naturally, is only true where the speed of the reaction is not considered; for substances often appear to be in equilibrium which are really changing, though very slightly. In other words, in the above statement we must recall our previous definition of the state of equilibrium. *When* ΔF *for a reaction is found to be negative* *in sign, it indicates that the reaction in question tends to go from left to right spontaneously.*

In accord with the above definition, it will be seen that from equation (18) considering (19) (where the value of the maximum work, W, *performed* by the process of transformation of N_1 moles of A_1 plus N_2 moles of A_2, both at a pressure equal to p_0 into N_1' moles of A_1' plus N_2' moles of A_2', both at the pressure p_0 is given), we have

$$-\Delta \mathrm{F} = W = RT \log_e K_p - RT \log_e \frac{p_0^{N_1'} p_0^{N_2'}}{p_0^{N_1} p_0^{N_2}}.$$

Assuming p_0 to be the standard pressure of one atmosphere, whereby the second term becomes equal to zero, we find

$$\Delta \mathrm{F} = -RT \log_e K_p,$$

i.e., the *increase in* free energy of a reaction can be found (so long as the gas laws hold) from its value of the equilibrium constant for pressures. ΔF is usually expressed in calories, R being taken, as we have considered it as 2, or more accurately as 1.9885 calories.

For the change in ΔF for any reaction with the temperature, i.e., to find the value of ΔF at one temperature for a reaction from its known value at some other temperature, and for an application of the concept of free energy in this form, see Lewis (Jour. Am. Chem. Soc., 35, 1, 1913) and Lewis and Burrows (*ibid.*, 34, 1515, 1912).

The effect of temperature upon an equilibrium. The variation of the criterion of equilibrium with the temperature.—In the case of an invariant equilibrium under constant pressure a change in the temperature causes one of the phases to disappear entirely. In the case of a univariant equilibrium, however, the effect is quite different. A very small change in temperature causes only a very slight change in the equilibrium. This causes a corresponding change in the relative composition of the reacting constituents, in one direction or the other, which just compensates the change which the equilibrium constant has suffered.

Before considering specific and numerical illustrations of the application of the law of mass action to chemical systems, we shall first investigate just how these constants, K_p and K_c, vary with the temperature, so that our later illustrations of this law may be more general and complete.

By differentiating equation (18) above, considering (19), since W and K_p are both functions of the temperature, T, we obtain,

$$\frac{dW}{dT}=R\log_e K_p+RT\frac{d(\log_e K_p)}{dT}-R\log_e\frac{{p_0}^{N_1'}{p_0}^{N_2'}}{{p_0}^{N_1}{p_0}^{N_2}}.$$

Combining this equation with the analytical expression of the second principle of thermo-dynamics (page 66), which can be written in the form $\frac{dW}{dT}=\frac{Q}{T}$, we find

$$Q=RT\log_e K_p+RT^2\frac{d(\log_e K_p)}{dT}-RT\log_e\frac{{p_0}^{N_1'}{p_0}^{N_2'}}{{p_0}^{N_1}{p_0}^{N_2}}.$$

This quantity, Q, is now the total heat absorbed by the system when the maximum work, W, is performed by the transformation of heat into work. Hence $Q-W$, when both are expressed in heat units, must be the amount of heat absorbed by the system and not transformed into work, but which remains as heat. Since the condition of the performance of external work has now been introduced by the use of the second principle, it is evident that the condition of this heat-difference is what we have designated as *at constant pressure*, and, further, since *it is conventional to designate an absorbed heat as negative* *in sign*, it is evident that for the quantity $Q-W$ we can substitute $-Q_p$, where Q_p *would be the heat* EVOLVED *by the reaction in going from left to right*, since K_p is written for that direction.

Subtracting W, as given by (18), from both sides of the above equation, remembering that $Q-W=-Q_p$, we find

$$-Q_p=RT^2\frac{d\,(\log_e K_p)}{dT},$$

or

$$\frac{d}{dT}(\log_e K_p)=\frac{-Q_p}{RT^2} \quad . \quad . \quad . \quad . \quad . \quad . \quad (22)$$

Since by (21) $K_c=K_p(RT)^{\Sigma N-\Sigma N'}$, i.e., K_c is equal numerically to K_p multiplied by RT raised to a power equal to the number of moles lost by the reaction going from left to right, as shown by the correctly written chemical equation, we have, substituting K_c for K_p in equation (22),

$$\frac{d}{dT}(\log_e K_c-\log_e (RT)^{\Sigma N-\Sigma N'})=\frac{-Q_p}{RT^2},$$

or

$$\frac{d}{dT}(\log_e K_c)-\frac{\Sigma N-\Sigma N'}{T}=\frac{-Q_p}{RT^2},$$

i.e.,

$$\frac{d}{dT}(\log_e K_c)=\frac{-Q_p}{RT^2}+\frac{\Sigma N-\Sigma N'}{T}=\frac{(\Sigma N-\Sigma N')RT-Q_p}{RT^2}.$$

But this term $(\Sigma N-\Sigma N')RT$, by definition, is simply an expression of the external work done upon, or by the system; hence, since it is identical with the term $-NRT$, as used on pages 236 and 237, we have, as there,*

$$-Q_p+(\Sigma N-\Sigma N')RT=-Q_v,$$

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* The N was taken there as equal to the difference between the final and original moles, i.e., as $\Sigma N'-\Sigma N$; consequently N was negative when moles were lost by the reaction going from left to right—here, under those conditions, it would be positive.

and we can write

$$\frac{d}{dT}(\log_e K_c) = \frac{-Q_v}{RT^2} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (23)$$

These differential equations (22) and (23) give us the relationship existing between the constants of a reaction, K_c or K_p, and the temperature, T, where Q is the heat *evolved* when the reaction goes from left to right. If Q_p or Q_v, appearing on the right side of a thermo-chemical equation, then, is positive in sign, its negative value will appear in the numerator of the term on the right; while if the sign on the right side is negative, its positive value will appear there.

Before putting these equations to practical use it is necessary to integrate them. In the first form of equation we shall obtain, which was originally derived by van't Hoff, we assume Q to remain constant with varying temperature, and integrate the expressions between the limits T' and T. In the final equations so obtained we should expect, then, to be restricted to the use of relatively small temperature intervals, for otherwise Q would be far from constant between the limits. As even for small intervals of temperature, Q may vary appreciably, it will be best always to assume Q as at a temperature which is the mean of the two extremes.

As the results of such an integration of (22) and (23), we find, transforming the logarithms to the base e into those to the base 10 (i.e., by multiplying the value of $\log_e$ by $\frac{1}{2.303}$)

$$\log K_p' - \log K_p = \frac{Q_p}{2.303 \times R}\left(\frac{1}{T'} - \frac{1}{T}\right), \quad . \quad . \quad (24)$$

and

$$\log K_c' - \log K_c = \frac{Q_v}{2.303 \times R}\left(\frac{1}{T'} - \frac{1}{T}\right), \quad . \quad . \quad (25)$$

where R can be taken as equal to 2 calories,* and the sign of Q_p or Q_v is the same as the sign of the heat of the chemical reaction when it is written on the right side of the thermochemical equation, since the ratios taken as K_p or K_c always contain the substances on the right in the numerator. The equation in this form (either for K_p or K_c) is known as *the van't Hoff equation.*

The heat evolved by a chemical reaction in going from left to right, at the average temperature $\frac{T'+T}{2}$, *under constant pressure (external work) conditions, i.e.,* Q_p, *can be calculated from the equilibrium constant for pressures* (K_p' *and* K_p) *at the two temperatures* (T' *and* T)*; or, knowing* Q_p, *and* K_p *at one temperature we can calculate the value of* K_p', *at the other.* And, in the same way, the heat of reaction at constant volume (no-external work condition), all other conditions being the same, can be calculated from the constants K_c' and K_c at T' and T; or one value of K_c can be calculated from Q_v and the value of the other K_c'.

As will be seen, this supplements what we have considered under thermochemistry, for it gives us a method of calculating heats of reaction indirectly from the equilibrium constants of that reaction at two temperatures, and without any calorimetrical aid.

One consequence of these formulas is of special interest and importance. If Q for any reaction is zero, it would indicate that the equilibrium constant does not change in value with the temperature, i.e., that we must have the same relative quantities of substances present and in equilibrium at all temperatures. Experiment shows, in this connection, that in accord with the law, the reaction between acetic acid and alcohol

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* The more accurate value of 1.9885 calories can be used here for R, as is often done, but since we have used 2 calories throughout the text, we shall continue its use here.

For another form of integration of this type of equation, see Lewis, Jour. Am. Chem. Soc., 28, 153, 1906.

(page 248), the mutual transformation of optical isomers, and a number of other processes which neither absorb nor evolve heat, all attain equilibrium states which are not displaced by a change in the temperature.

Nernst has obtained another solution of the differential equation (22) above, by an integration in the form of a series; but as all the coefficients employed are known now in but a few isolated cases, he offers another equation relating K_p, Q_p and T, which is known as the *Nernst approximation formula*. Changing the notation to agree with that we have been using, this formula is

$$\log K_p = \log \frac{{p'}_1^{N'_1} {p'}_2^{N'_2}}{p_1^{N_1} p_2^{N_2}} = \frac{Q_p}{4.571T} + (\Sigma N' - \Sigma N) 1.75 \log T + (\Sigma N'C' - \Sigma NC),$$

in which $R = 1.985$ calories, thus leading to the 4.571 in place of the 4.606 when $R = 2$. Here the term $\Sigma N' - \Sigma N$ gives the number of moles *formed* when the reaction goes from left to right, the ratio K_p giving the substances formed (right side) in the numerator; and Q_p is the heat *evolved* under constant pressure and at room temperature, when the reaction goes to the right; in other words Q_p has here the same sign as it would have written on the right side of the thermo-chemical equation. The terms C and C' in $\Sigma N'C' - \Sigma NC$ are the so-called "chemical constants" of the constituents of the reaction; $\Sigma N'C' - \Sigma NC$ being found by multiplying the specific value of the constant for each constituent, by the number of moles to which it appears in the chemical equation, and subtracting the summation of these for the original substances on the left (ΣNC) from that of those of the final products on the right ($\Sigma N'C'$). Some of the known values for the "chemical constant" are given in the table on the following page:

"CHEMICAL CONSTANTS"

H_2 1.6	HCl 3.0	HI 3.4
CH_4 2.5	NO 3.5	CS_2 3.1
N_2 2.6	N_2O 3.3	NH_3 3.3
O_2 2.8	H_2S 3.0	N_2O 3.6
CO 3.5	SO_3 3.0	CCl_4 3.1
Cl_2 3.1	SO_2 3.3	$CHCl_3$ 3.2
I_2 3.9	CO_2-3.2	C_6H_6 3.0

As will be seen, the average value here is about 3.1; the lower boiling constituents having smaller values.*

Applications of the law of mass action, and of the equations of van't Hoff and Nernst.

HOMOGENEOUS GASEOUS SYSTEMS

To show how well experimental observation confirms the relationships derived above, the application of the various equations is made below to the equilibrium state, under different conditions, of that most important, industrial, reaction

$$2SO_3 \rightleftarrows 2SO_2+O_2.$$

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* The above equation is also written in the form

$$\log K_p{}^* = \log \frac{{p_1}^{N_1}{p_2}^{N_2}}{{p'_1}^{N'_1}{p'_2}^{N'_2}} = \frac{-Qp}{4.571T} + (\Sigma N - \Sigma N')\ 1.75 \log T + (\Sigma NC - \Sigma N'C'),$$

which of course would ultimately give the value of K_p found from the other, for this unconventional log K_p* (with the substances on the *left* in the numerator) is plainly equal to the negative value of the log of the conventional K_p (with the substances on the right in the numerator) we have been using. Q_p, here, naturally has the sign of Q_p as written on the left side of the thermo-chemical equation considered.

In using equations of this form, and empirical equations similar to these are in very general use, care must be taken to observe a rule with respect to these logarithms to the base 10. When in calculating a value of K_p, for example, we find that log $K_p = -3.7635$, the number on the right being negative in sign, it is necessary before seeking the antilogarithm to get the value K_p, to transform the negative logarithm into one with a *positive mantissa*, for in its present state this is negative and its value cannot be found from our tables. To make this transformation, we simply add 1 to the mantissa and subtract 1 from the characteristic, and obtain in the above case $\bar{4}.2365$, which gives, by aid of a table of logarithms, $K_p = 0.0001724$.

Naturally, it does not matter here whether we consider the reaction as one forming SO_3, or whether we treat it as a dissociation of SO_3 into SO_2 and O_2; for the final results obtained in either way will enable us to fix the final equilibrium, which as the common limit of two inverse reactions, must be identical.

In finding the amounts of the three constituents present at equilibrium at the various temperatures Bodenstein and Pohl (Zeit. für Elektrochem. **11**, 373, 1905) employed platinized asbestos as catalytic agent, and established the equilibrium, not only from the SO_3 side, and with equivalent amounts of SO_2 and O_2, but also with an excess first of one and then of the other of these, and finally with these in the presence of various amounts of the inert gas nitrogen. In all cases, however, as should be according to the law, the equilibrium constant was found to be the same, within the experimental error.

In the table below are some of the results found at the constant temperature of 727° C., or 1000° absolute, under the constant total pressure of 1 atmosphere.

$$2SO_3 \rightleftarrows 2SO_2+O_2$$

$T=1000°$; total pressure of 1 atmosphere

At Equilibrium *						$K_c = \frac{c^2_{SO_2} c_{O_2}}{c^2_{SO_3}}$	$K_p = \frac{p^2_{SO_2} p_{O_2}}{p^2_{SO_3}}$
Relative Moles × 10^4.			Partial Pressures (atmos.)				
SO_2	SO_3	O_2	SO_2	SO_3	O_2		
15.9	17.5	18.2	.308	.339	.353	0.00355	0.290
218	174	85.8	.456	.364	.180	0.00344	0.282
369	287	130	.470	.365	.165	0.00333	0.274
260	192	88.7	.481	.355	.164	0.00367	0.301
388	230	69.8	.564	.334	.102	0.00360	0.296
252	148	44.9	.566	.333	.101	0.00357	0.293
178	212	261	.273	.326	.401	0.00345	0.283
					Av.	0.00352	0.288

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* The partial pressures here are calculated from the moles; and K_p from K_c by $K_c=K_p(0.08204\times1000)^{-1}$, but the same values (practically) will be given direct from the pressures as given.

As the temperature is increased in the case of this reaction, the constant, K_c or K_p, as written above is found to increase in value, as will be seen from the following experimental values of K_c: *

$t°$	$T°$	K_c
528	801	1.55×10^{-5}
627	900	3.16×10^{-4}
727	1000	3.52×10^{-3}
832	1105	2.80×10^{-2}
897	1170	8.16×10^{-2}

Since we know the equilibrium constants for concentrations now at a number of temperatures, it is of course possible to apply to them the van't Hoff equation. Here the temperature interval is rather larger than should be used in general, on the assumption made in the integration that Q_v does not change very considerably between the temperature limits. In this specific case, however, Q_v apparently is nearly independent of the temperature, as will be seen from the results, so the temperature intervals are not too large to be employed here.

THE VAN'T HOFF EQUATION APPLIED TO $2SO_3 \rightleftarrows 2SO_2 + O_2$

T.	K_c.	ΔT.	Q_v in $2SO_3 \leftrightarrows 2SO_2 + O_2 + Q_v$.
801	1.55×10^{-5}	99	$-43{,}930$
900	3.16×10^{-4}	100	$-43{,}390$
1000	3.52×10^{-3}	95	$-43{,}650$
1105	2.80×10^{-2}	65	$-42{,}560$
1170	8.16×10^{-2}		Mean $-43{,}383$ calories

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* The value of $K_c \left(= \frac{c^2_{SO_2} c_{O_2}}{c^2_{SO_3}} \right)$ at any desired temperature can be found very closely from the empirical equation $\log K_c = -\frac{10373}{T} - 2.222 \log T + 14.585$.

Here the values of Q_v are found by taking the K_c values at the different temperatures in pairs, and we find, in average,

$$2SO_3 \rightleftarrows 2SO_2+O_2-43{,}383 \text{ calories at constant volume,}$$

where $-43{,}100$ was found experimentally at 17° C. Since the value of Q_v does not appear to vary with a change in the temperature, it would mean that the specific heat at constant volume for two moles of SO_3 is about equal to the specific heat of two moles of SO_2, plus that of one mole of oxygen, both under constant volume conditions.

The value of Q_v, above, is of course the value of Q which is to be placed on the right side of that thermochemical equation which is employed in finding the value of K_c' and K_c, i.e., the above equation in this case. Naturally, if the K values were found for the equation $SO_3 \rightleftarrows SO_2+\frac{1}{2}O_2$, we would have $K_c=\frac{c_{SO_2}c^{\frac{1}{2}}_{O_2}}{c_{SO_3}}$, and the Q_v found would be for the reaction involving 1 mole of SO_3, i.e., it would be one-half the value of the former.

The change in the value of K_c observed experimentally for the reaction $2SO_3 \rightleftarrows 2SO_2+O_2$ gives us a verification of *the theorem* of Le Chatelier, as far as concerns the sign of the heat involved in a chemical equation, and the effect of a change of temperature upon the direction of that reaction. According to that theorem, the side of the reaction which absorbs heat should be favored by an increase of temperature; and that which evolves heat should be favored by a decrease of temperature. Since the value of K_c here increases with increased temperature, the right side of the equation is shown to be favored by the increase, i.e., $2SO_2+O_2$, for in $K_c=\frac{c^2_{SO_2}c_{O_2}}{c^2_{SO_3}}$ that is in the numerator, and consequently must increase in amount with increased temperature. Therefore the sign of Q_v on the right side of the above chemical equation must be negative, i.e., heat is absorbed, and we must have $2SO_3 \rightleftarrows 2SO_2 + O_2 - Q_v$. Calorimetrical experiments also confirm this.

We can also foresee that the above relations, as found by aid of Le Chatelier's theorem, must be true, by a glance at the equation of van't Hoff, viz.:

$$\log K_c' - \log K_c = \frac{Q_v}{2.303R}\left(\frac{1}{T'} - \frac{1}{T}\right).$$

Here if T' is assumed to be the higher temperature, at which K_c' holds, and K_c' is found also to be larger than K_c as found at the lower temperature T, Q_v must be negative, for it is the reciprocals of the T values which are considered, and the sign of the term involving the T values will be negative. If K_c decreased with an increase of temperature, on the other hand, the signs of both the K and T terms will be the same, and Q_v would be positive; i.e., heat would be evolved by the formation of the substances on the right, and they would combine to a greater extent at higher temperatures than at lower ones.

Politzer has applied the approximation formula of Nernst to the equilibrium of SO_3, SO_2 and O_2. Experimentally, it is observed that the heat evolved when 2 moles of SO_3 are formed at 17° is 43,100 calories. Hence in

$$\log K_p = \log \frac{p^2_{SO_2} p_{O_2}}{p^2_{SO_3}} = \frac{Q_p}{4.571T} + (\Sigma N' - \Sigma N)1.75 \log T + (\Sigma N'C' - \Sigma NC),$$

$Q_p = -43,100$, since if placed on the right side of the equation, as given in the numerator of K_p, it would have the opposite sign, $\Sigma N' - \Sigma N$, in $2SO_3 \rightleftarrows 2SO_2 + O_2$, would be equal to $2 + 1 - 1 = 1$, and $\Sigma N'C' - \Sigma NC$, by page 264, is equal to $2 \times 3.3 + 2.8 - 2 \times 3.0 = 3.4$, and we have

$$\log K_p = \frac{-43,100}{4.571T} + 1.75 \log T + 3.4.$$

Substituting in this equation the value of K_p at 1000° absolute (page 265), viz., 0.29, we find that the absolute temperature corresponding to it is 1024° in place of the 1000°. The values of K_p calculated from this equation, while of the same order, differ considerably from the experimental values. This is due to the fact it is the whole numbers, in this logarithmic relation, which fix the order of K_p, but the decimal part which fixes its exact value.

While the above shows clearly that the relationships we have derived hold experimentally for a system, no matter how much of an excess of one of the constituents we may have started with, or whether or not an inert gas is also present, or what the temperature may be, so long as it remains constant—it does not show some of the possible applications of the law of mass action, especially those having to do with the effect of increased or decreased pressure upon the system. Nor does it make clear how we can trace the effect of an added constituent upon the equilibrium state of the system. These things we shall now consider.

If we start, for example, with a mixture of nitrogen and hydrogen, under 1 atmosphere pressure, which contains 1 mole of nitrogen to every 3 moles of hydrogen, it is found experimentally that the final amounts of nitrogen and hydrogen remaining, and that of ammonia formed, at equilibrium, at 27° and 327° C., are

t	Vol. % H_2	Vol. % N_2	Vol. % NH_3
27	2.76	0.92	96.32
327	73.75	24.58	1.67

The chemical reaction here is

$$N_2+3H_2 \rightleftarrows 2NH_3,$$

or

$$\tfrac{1}{2}N_2+\tfrac{3}{2}H_2 \rightleftarrows NH_3;$$

so that the criteria of equilibrium for pressures and concentrations are

$$K_p = \frac{p^2_{NH_3}}{p_{N_2} p^3_{H_2}}; \qquad K_c = \frac{c^2_{NH_3}}{c_{N_2} c^3_{H_2}}.$$

and

$$\mathbf{K}_p = \frac{p_{NH_3}}{p^{\frac{1}{2}}_{N_2} p^{\frac{3}{2}}_{H_2}}; \qquad \mathbf{K}_c = \frac{c_{NH_3}}{c^{\frac{1}{2}}_{N_2} c^{\frac{3}{2}}_{H_2}}.*$$

Since the values in the table above are percentages by volume, they must also be equal to the fractional moles in a total amount equal to 100 moles; as well as to the partial pressures in atmospheres, when the total amount is in such a volume that at the temperature in question the total pressure is 100 atmospheres, since their total is equal to 100. From these facts we can now find the numerical values necessary to calculate the value of any of the above K terms.

Substituting the values at 27° (after division by 100) directly as partial pressures in atmospheres in a total pressure of 1 atmosphere, in the K_p and $\mathbf{K}_p$ equations, we find $K_p = 47.96 \times 10^5$ and $\mathbf{K}_p = 21.91 \times 10^2$; and since these same numbers are then also the fractional moles in a total of 1 mole, the concentrations are $c_{N_2} = \dfrac{0.0092}{1 \times 22.4 \times \dfrac{300}{273}}$, $c_{H_2} = \dfrac{0.0276}{1 \times 22.4 \times \dfrac{300}{273}}$ and

$$c_{NH_3} = \frac{0.9632}{1 \times 22.4 \times \frac{300}{273}}, \quad K_c = 29.05 \times 10^8 \text{ and } \mathbf{K}_c = 53.92 \times 10^3.$$

The effect of temperature on this reaction is especially striking and characteristic. Thus at 27° we have NH_3 always in excess, while at 327° the N_2 and H_2 are always present to the greater extent. This is shown in the values of K at the two temperatures, just as it is in the results in the above table. Using the figures for 327° we find $K_p=28.28\times10^{-4}$, $\mathbf{K}_p=53.18\times10^{-3}$ and since the concentrations are $\dfrac{0.0167}{1\times22.4\times\frac{600}{273}}$ for NH_3, $\dfrac{0.7375}{1\times22.4\times\frac{600}{273}}$ for H_2, and $\dfrac{0.2458}{1\times22.4\times\frac{600}{273}}$ for N_2, $K_c=68.55\times10^{-1}$ and $\mathbf{K}_c=26.18\times10^{-1}$.

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* Here, of course, $K_c = K_p(RT)^2$ and $\mathbf{K}_c = \mathbf{K}_p(RT)$, by equation (21). The results calculated by either form would, naturally, be identical, but it is sometimes simpler mathematically to use the second form, i.e., $\mathbf{K}_p$ or $\mathbf{K}_c$.

It is plain here, from the K equations, that if one of the original products be present in an excess, over the quantity which can coexist at equilibrium with the present amounts of the others, or if one of the products be added to the system already in equilibrium, the reaction must go further, for the denominator of the K ratio would then be too great for equilibrium to exist, and a rearrangement, i.e., a union of further N_2 and H_2 to form NH_3 must take place, decreasing the denominator, and consequently by the chemical action increasing the numerator, until the original value of the criterion of equilibrium, K, is again attained. Naturally we can follow this rearrangement without difficulty, for the only changes possible are those which take place according to the chemical equation. For example let us imagine that we start at 27° with 0.5 mole of hydrogen, 0.2 mole of nitrogen and 0.3 mole of ammonia and calculate the number of moles of each of these substances which will be present after the equilibrium state is attained under the constant pressure of 1 atmosphere. Let us assume that $2x$ moles of ammonia have been formed when equilibrium is established. According to the chemical reaction

$$N_2+3H_2\rightleftarrows 2NH_3,$$

then we must have lost x moles of N_2 and $3x$ of H_2, and the constituent moles at equilibrium will be $0.2-x$ of nitrogen,

$0.5-3x$ of hydrogen, and $0.3+2x$ of ammonia. The summation of these moles, since the total pressure is atmospheric and constant and the temperature is 27° C., will occupy the volume, $F.V=(1+2x)22.4\times\frac{300}{273}$ liters.

We are now in position to state either the concentrations or partial pressures of the substances coexisting in equilibrium, and consequently by the substitution of these in the ratio of the criterion of equilibrium, the numerical and constant value of which is known, we can solve for the unknown term x, the extent of displacement of the system (in terms of nitrogen) attaining in equilibrium.

Let us consider the chemical equation as given above and employ the partial pressure form (although naturally the other would lead to an identical result). Substituting the partial pressures, $p_{NH_3}=\frac{0.3+2x}{1+2x}\times 1$; $p_{N_2}=\frac{0.2-x}{1+2x}\times 1$; $p_{H_2}=\frac{0.5-3x}{1+2x}\times 1$ in $K_p=\frac{p^2_{NH_3}}{p_{N_2}p_{H_2}^3}$ we find

$$K_p=47.96\times 10^5=\frac{\left(\frac{0.3+2x}{1+2x}\right)^2}{\left(\frac{0.2-x}{1+2x}\right)\left(\frac{0.5-3x}{1+2x}\right)^3}.$$

The value of x, here, if positive in sign (i.e., if NH_3 is formed) cannot be greater than 0.167, for if it were we should be losing more hydrogen than we have present; while if negative in sign (i.e., NH_3 is lost) cannot be greater than 0.15 without using up more ammonia than we have (and it cannot be as great as 0.15, for if the ammonia were all removed we should no longer have an equilibrium state). Although mathematically we we cannot solve such an equation for all its roots, it is possible to find the chemical root, i.e., the change x (either + or −) which would lead to equilibrium, by a method of trial and approximation. In general in the solution of all such equations for chemical purposes, the *smallest* possible root is the only one to be considered, for if a loss or gain of a minimum value could produce equilibrium, it is inconceivable that after the system had attained equilibrium by that change, it could go again, and of itself, out of that state to produce another equilibrium state, involving a larger change.

Since in the above illustration we assumed a total constant pressure of 1 atmosphere in the system, the effect of a change to some other, constant, pressure upon the system is not shown. Let us now assume that we start with 1 mole of NH_3 at 27° under 0.1 atmosphere total pressure, and causing that to remain constant, calculate the degree of dissociation of NH_3 under these conditions. If we designate the degree of dissociation of NH_3 by y, we would have $1-y$ of NH_3, $\frac{1}{2}y$ of N_2 and $\frac{3}{2}y$ of H_2, according to the reaction.

$$\tfrac{1}{2}N_2+\tfrac{3}{2}H_2 \rightleftarrows NH_3,$$

or a total of $1+y$ moles produced from the original 1 mole of NH_3. The partial pressures here would then be $\frac{1-y}{1+y}\times 0.1$ for NH_3, $\frac{\frac{3}{2}y}{1+y}\times 0.1$ for H_2 and $\frac{\frac{1}{2}y}{1+y}\times 0.1$ for N_2, and y must have such a value (positive in sign here, naturally) as to satisfy the equation

$$\mathbf{K}_p = 21.91\times 10^2 = \frac{\left(\frac{1-y}{1+y}\times 0.1\right)}{\left(\frac{\frac{1}{2}y}{1+y}\times 0.1\right)^{\frac{1}{2}}\left(\frac{\frac{3}{2}y}{1+y}\times 0.1\right)^{\frac{3}{2}}}.$$

Since the 0.1 here represents the total pressure which is held constant over the system, it is plain that we can express the percentage of dissociation, y, of NH_3 under any constant pressure, p, in terms of the pressure, at 27° C., by substituting p for 0.1. We find in this way, simplifying the equation,

$$21.91 \times 10^{-2} = \frac{(1-y)(1+y)}{(\frac{3}{2}y)^{\frac{3}{2}}(\frac{1}{2}y)^{\frac{1}{2}}p}.$$

From this equation we see, since $\mathbf{K}_p$ $(=21.91 \times 10^{-2})$ always remains constant under any conditions, so long as the temperature is 27°, that the effect of pressure upon the relative amounts of the substances which can coexist at equilibrium will be such that high pressure will necessitate the decrease in the amounts in the denominator (to retain the ratio constant), i.e., high pressure will favor the formation of the NH_3, while low pressure will necessitate an increase in the amounts in the denominator, i.e., will favor the formation of N_2 and H_2 at the expense of the NH_3. Naturally, here, the decrease or increase of the denominator does not do all the regulation of the ratio directly, for at the same time the loss of N_2 and H_2 means a gain in NH_3 by the chemical reaction, and *vice versa*. These two actions together, then, would cause the criterion of equilibrium to be ultimately fulfilled in all such cases.

As will be seen, the above is simply a confirmation of the theorem of Le Chatelier, referred to pressure, for by that, high pressure would favor the side of smaller volume (viz., NH_3); and low pressure would favor the side of larger volume (viz., N_2-H_2). Numerical confirmations of this fact will be found in the answers to some of the problems in Chapter X under this heading.

The variation in the experimental value of the constant $\mathbf{K}_p$ here with the temperature can be represented by the equation

$$\log \mathbf{K}_p = \frac{2215}{T} - 3.626 \log T + 3.07 \times 10^{-4} T + 0.29 \times 10^{-6} T^2 + 4.82.^*$$

---

* All terms, no matter how small they may seem, in such equations as this must be included in the solution for K_p, as the decimal portion is the mantissa

From this equation, as well as from the table above, it will be seen that **K**$_p$ decreases with increased temperature, i.e., that the higher the temperature, the larger will be the denominator (and the smaller will be the numerator) of the ratio; which means that the larger will be the amounts of N_2 and H_2 in the equilibrium state, as compared to that of NH_3. Here, then, just as for the equilibrium of $SO_3-SO_2-O_2$ according to the van't Hoff equation, it can be shown that the heat involved in the thermo-chemical equation must be negative on the H_2-N_2 side, i.e., heat must be evolved by the formation of NH_3. This is also found to be the case by experiment; and again could be forecasted by the theorem of Le Chatelier, for since heat is evolved on the NH_3 side, high temperature would favor the increased formation of H_2 and N_2; and low temperature would favor the NH_3 side; and as this is the behavior of the reaction as observed experimentally, heat must be evolved when NH_3 is formed.

It is not only to such dissociation phenomena, considered either as a dissociation of a single substance, or as a union of the constituent substances to form that single substance, that the law of mass action and its criterion of equilibrium can be applied—for it is applicable to *all* chemical reactions, however complicated. Let us consider, for example, the chemical reaction involved in the Deacon process for the production of chlorine, viz.,

$$4HCl+O_2 \rightleftarrows 2H_2O+2Cl_2,$$

for which, at any one temperature, if the terms p are those observed in the equilibrium state, we have

$$K_p=\frac{p^2_{H_2O}p^2_{Cl_2}}{p^4_{HCl}p_{O_2}},$$

---

of the logarithm, i.e., fixes the actual number; the characteristic showing the order of magnitude only.

the numerical value of K_p varying with the temperature according to the equation

$$\log K_p = \frac{5750}{T} - 2.136 \log T - 8.57 \times 10^{-4}T + 6.83 \times 10^{-8}T^2 + 0.296.$$

Employing any one constant temperature, T, at which the value of K_p is known, let us imagine that we start with 0.62 mole of HCl, 0.95 of O_2, 0.83 of H_2O and 0.03 of Cl_2, the system to remain throughout at the constant pressure of 1 atmosphere, and find the direction and extent of the reaction which takes place in carrying the system from this state to one of equilibrium. Here we shall employ the K_c form of formula, calculating the final concentrations in terms of an assumed change in moles, z, which we shall take to be the moles of HCl lost during the reaction. First, of course, we must transform the known value of K_p into its corresponding form K_c. This we do by aid of equation (21), viz.:

$$K_c = K_p(RT)^{5-4}.$$

It is plain here that the moles present in equilibrium in terms of the original ones and the assumed change, will be $0.62 - z$ for HCl, $0.95 - \frac{1}{4}z$ for O_2, $0.83 + \frac{1}{2}z$ for H_2O, and $0.03 + \frac{1}{2}z$ for Cl_2. In total, then, we shall have $(2.43 - \frac{1}{4}z)$ moles, in the volume $\text{F.V.} = (2.43 - \frac{1}{4}z)22.4\frac{T}{273}$ liters, since the pressure is held constant at 1 atmosphere. Substituting the number of moles of the constituents, each divided by this final volume, for the terms c in our K_c equation, we find

$$K_c = \frac{c^2_{H_2O}c^2_{Cl_2}}{c^4_{HCl}c_{O_2}} = \frac{\left(\frac{0.83 + \frac{1}{2}z}{\text{F. V.}}\right)^2 \left(\frac{0.03 + \frac{1}{2}z}{\text{F. V.}}\right)^2}{\left(\frac{0.62 - z}{\text{F. V.}}\right)^4 \left(\frac{0.95 - \frac{1}{4}z}{\text{F. V.}}\right)},$$

from which we could find by a method of trial the minimum value of z which would satisfy the equation, and from that the amount of each constituent at equilibrium. If the sign of z should prove to be negative, we would know that the reaction would go to form HCl and O_2, in place of causing these to disappear, as we assumed at the start—and the numerical value of z would of course give us the extent of the reaction in terms of a loss or gain in HCl.

Thus far in our illustrations, we have considered only those reactions taking place under constant pressure conditions—but, naturally, reactions taking place in unchanged volume, i.e., with a change of pressure, could be handled just as readily. In such a case, as in the others, it is simply a question of finding expressions for the partial pressures or concentrations under those conditions, and then substituting these in the K_p or K_c equation, for the numerical value of the K term remains unchanged so long as the temperature is held constant.

For example in the illustration of the Deacon process, if we had started as we did there at atmospheric pressure and then assumed the reaction to take place (in a constant volume equal to that which would be occupied by the original amounts (2.43 moles in total) at T and 1 atmosphere, if they did not react), we would find that it would not proceed to the extent (toward the right) that it did before. Since the substances on the right occupy a smaller volume than those on the left (i.e., since there are but 4 moles on the right side produced by the loss of 5 moles on the left) the pressure, *in constant volume*, must *decrease* by the reaction going to the right. This decrease in pressure, however, would favor the persistence of the substances on the left—hence less of the products on the right would be formed at constant volume than under a constant pressure of 1 atmosphere. This can perhaps be made clearer by the assumption that w moles of HCl are lost in place of z above, and the substitution of this for z in the above equation, also substituting the present final (also original) volume $\left(=2.43\times 22.4\times\frac{T}{273}\right)$ for the F. V. used there.

The partial pressures of the constituents in this case can be found as soon as we know the total pressure produced by the assumed change w. Since by assumption the original 2.43 moles were present in such a volume to give 1 atmosphere pressure at the temperature in question, and $2.43-\frac{1}{4}w$ moles are now present in the same volume, at the same temperature, the total final pressure can be found from the proportion $2.43 : 2.43-\frac{1}{4}w :: 1 : p$, i.e., $p=\frac{2.43-\frac{1}{4}w}{2.43}$ atmos. The partial pressures in the two illustrations, then, are:

At Constant Pressure	In Constant Volume
$p_{HCl}=\frac{0.62-z}{2.43-\frac{1}{4}z}\times 1$	$p_{HCl}=\frac{0.62-w}{2.43-\frac{1}{4}w}\times\frac{2.43-\frac{1}{4}w}{2.43}$
$p_{O_2}=\frac{0.95-\frac{1}{4}z}{2.43-\frac{1}{4}z}\times 1$	$p_{O_2}=\frac{0.95-\frac{1}{4}w}{2.43-\frac{1}{4}w}\times\frac{2.43-\frac{1}{4}w}{2.43}$
$p_{H_2O}=\frac{0.83+\frac{1}{2}z}{2.43-\frac{1}{4}z}\times 1$	$p_{H_2O}=\frac{0.83+\frac{1}{2}w}{2.43-\frac{1}{4}w}\times\frac{2.43-\frac{1}{4}w}{2.43}$
$p_{Cl_2}=\frac{0.03+\frac{1}{2}z}{2.43-\frac{1}{4}z}\times 1$	$p_{Cl_2}=\frac{0.03+\frac{1}{2}w}{2.43-\frac{1}{4}w}\times\frac{2.43-\frac{1}{4}w}{2.43}$

When substituted in $K_p=\frac{p^2_{H_2O}p^2_{Cl_2}}{p^4_{HCl}p_{O_2}}$, i.e., equated to the same K_p value, these terms p will show the amounts present in equilibrium in the two cases, i.e., will lead to the values of z and w.

Calling the term, $\frac{2.43-\frac{1}{4}w}{2.43}$, p, and simplifying the expression as we did in the case of NH_3, we find the effect of any constant pressure on the above reaction to be given by the equation,

$$K_p=\frac{\left(\frac{0.83+\frac{1}{2}w}{2.43-\frac{1}{4}w}\right)^2\left(\frac{0.03+\frac{1}{2}w}{2.43-\frac{1}{4}w}\right)^2}{\left(\frac{0.62-w}{2.43-\frac{1}{4}w}\right)^4\left(\frac{0.95-\frac{1}{4}w}{2.43-\frac{1}{4}w}\right)p};$$

from which as will be seen that low values of p will favor the formation of the $HCl-O_2$ side, while high pressure will favor the H_2O-Cl_2 side. The term w here, of course, is now simply the loss of HCl (either positive or negative) observed when the original amounts given above react to form equilibrium at any constant pressure, p.

In case we are considering constant volume conditions, the simplest possible case would be one where the amounts of the original substances are given in terms of partial pressure, for then (*but then only*) the partial pressures of the constituents, at that temperature, can only change by the progress of the chemical reaction itself. Thus in case of the reaction

$$2CO_2 \rightleftarrows 2CO + O_2$$

we find at 3000° and atmospheric pressure that $\alpha = 0.4$, from which it is evident that at equilibrium we have $2(1-0.4)$ moles of CO_2, 2×0.4 of CO, and 0.4 of O_2, or 2.4 moles in total, hence

$$p_{CO_2} = \frac{2(1-0.4)}{2.4} \times 1;\ p_{CO} = \frac{2 \times 0.4}{2.4} \times 1 \text{ and } p_{O_2} = \frac{0.4}{2.4} \times 1$$

in atmospheres, and

$$K_p = \frac{p^2_{CO} p_{O_2}}{p^2_{CO_2}} = 0.074.$$

If now we should assume that we start with a partial pressure of 0.354 atmosphere of CO_2, 0.43 of CO, and 0.6 of O_2, and retain the system at *constant volume* * and 3000° C., calling x the loss in partial pressure of the CO_2 necessary to take the system into the equilibrium state, the final, equilibrium, partial pressures will be $0.354 - x$ for CO_2, $0.43 + x$ for CO, and $0.6 + \frac{1}{2}x$ for O_2, all in atmospheres and we would have

$$0.074 = \frac{(0.43+x)^2(0.6+\frac{1}{2}x)}{(0.354-x)^2};$$

---

* The volume being equal to that in which each of the original substances at 3000° would give these pressures, if they did not react.

from which x, also in atmospheres, can be estimated, and consequently the partial pressures of the constituents calculated.

This form, however, can only be used where constant volume is the assumed condition, for a change in volume by the reaction, under constant pressure, would change the partial pressures so that we could not readily represent them as above, for not only the term x, but also the original pressures, would change by the change in volume. When we start with partial pressures, and assume the total *pressure* to remain constant, we must first transform the partial pressures given into moles per liter $\left(c=\frac{p}{RT}\right)$, and then, assuming one liter, treat the problem exactly as those above when moles are given. Since the 1 liter assumed will contain the number of moles it must to give the constant pressure, p, over the system, the new number of moles found at equilibrium will give the correct volume, without further thought from the relationship

$$\text{F.V.} = \text{moles} \times 22.4 \times \frac{T}{273} \times \frac{760}{p},$$

where the pressure p is in millimeters of mercury.

A simplification of the use of the criteria of equilibrium is also observed in the case of such reactions as

$$2\text{HI} = \text{H}_2 + \text{I}_2,$$

where

$$K_c = \frac{c_{\text{H}_2} c_{\text{I}_2}}{c^2_{\text{HI}}} \quad \text{or} \quad K_p = \frac{p_{\text{H}_2} p_{\text{I}_2}}{p^2_{\text{HI}}}.*$$

Here since the numbers of moles on the two sides are the same, there is no change in volume by the progress of the reaction in either direction. And as will be seen from these K ratios, any term to transform c into p would cancel in the ratio, since

* $K_c = K_p(RT)^0 = K_p.$

it would be raised to the same power in both numerator and denominator. This, of course, means that not only is K_c equal to K_p numerically, but that any term proportional to concentration or partial pressure could be substituted for these without changing the value of $K_c = K_p$. In fact, here, we can substitute the volumes of the constituents, all measured separately at the same pressure and temperature, and then mixed, for either the c or p terms, still employing the identical value of $K_c = K_p$.

An idea of the *physical significance* of the criterion of equilibrium can be obtained for a simple chemical reaction (1 mole forming 2 moles) in the following way. The constant for concentrations of the reaction

$$PCl_5 \rightleftarrows PCl_3 + Cl_2,$$

where we start with 1 mole of PCl_5, which is dissociated at T and 1 atmosphere pressure to the extent α, α being the percentage of the 1 here, is plainly

$$K_c = \frac{\left(\frac{\alpha}{\text{F. V.}}\right)\left(\frac{\alpha}{\text{F. V.}}\right)}{\frac{1-\alpha}{\text{F. V.}}} = \frac{\alpha^2}{(1-\alpha)\ \text{F. V.}},$$

where F. V. is the final volume of the system, i.e., $(1+\alpha)22.4\frac{T}{273}$ liters. If we now assume α to be 0.5, we find

$$K_c = \frac{(0.5)^2}{(1-0.5)\ \text{F. V.}},$$

or

$$2K_c = \frac{1}{\text{F. V.}}.$$

The dissociation constant for concentrations of a reaction of the type $AB \rightleftarrows A+B$, *at any temperature, then, is of such a value that when multiplied by 2 it is equal to the reciprocal of the final volume, which, under 1 atmosphere pressure at that temperature, is occupied by the gaseous system produced by the dissociation of 1 mole of AB to the extent of 50%.* A similar application might also be made to more complicated reactions, but the result would then also be more complex. At any rate the above will give an idea of what the criterion of equilibrium means physically.

Non-homogeneous systems.—The application of the criterion of equilibrium to non-homogeneous systems, i.e., those containing solids or liquids as well as gases, is much simpler than is the case for homogeneous ones, for the solid or liquid present at any one temperature will be constant in effect, and so long as it continues present, this constant effect of it can be included in the constant of the law of mass action, giving us a new constant which can be treated exactly as the K_c or K_p would be.

In the case of the physical reaction

$$H_2O \text{ liquid} \rightleftarrows H_2O \text{ gaseous},$$

we know that at any one temperature the pressure of water vapor is constant, independent of the actual amount of liquid water present, hence we have

$$\text{constant}_p = p_{\text{vapor}}$$

and this " constant_p " can be treated in every way as K_p would; in other words, two values of this at two temperatures could be substituted in the van't Hoff equation and the heat of evaporation of water at the average temperature and under constant pressure, calculated from it. In case a term, to be used as

K_c would be, is sought, we have simply to transform p into c, i.e.,

$$\text{constant}_c = c_{\text{vapor}} = \frac{p_{\text{vapor}}}{RT},$$

where, as in all such equations, p must be in atmospheres, R in liter atmospheres, if we are to find c in moles per liter.

In a similar way the chemical reaction

$$CaCO_3 \text{ (solid)} \rightleftarrows CaO \text{ (solid)} + CO_2 \text{ (gaseous)},$$

leads by the law of mass action to

$$K_p = \frac{p_{CaO}\,p_{CO_2}}{p_{CaCO_3}}$$

or, since the effect of the $CaCO_3$ and CaO are constant at any one temperature, independent of the amounts present,

$$\frac{K_p\,p_{CaCO_3}}{p_{CaO}} = \text{constant}_p = p_{CO_2}; \quad \text{or} \quad \text{constant}_c = \frac{p_{CO_2}}{RT},$$

i.e., equilibrium at any one temperature depends only upon the pressure or concentration of the carbon dioxide gas produced.

And again here these values at two temperatures would lead in the van't Hoff equation to the heat of dissociation of $CaCO_3$.

In the table below the pressures are given under which equilibrium exists at different temperatures in the case of this system:

EQUILIBRIUM OF $CaCO_3 \rightleftarrows CO_2 + CaO$

Temperature ° C.	Press. mms. of Hg.	Temperature ° C.	Press. mms. of Hg.
547	27	745	289
610	46	810	678
625	56	812	753
740	255	865	1333

This means that $CaCO_3$, when heated to any temperature, gives off CO_2, $CaCO_3$, and CaO until a certain pressure of CO_2 is reached. Thus at 547° C. a pressure of 27 mms. of mercury is produced.

In the following table are given the temperatures at which various substances begin to break down, forming non-homogeneous equilibria, and also those temperatures at which the process is complete (Hempel and Schubert, Zeit. f. Elektrochem., 18, 729, 1912).

Substance.	$t°$ at which Dissociation Begins.	$t°$ at which Dissociation is Complete.
MnO_2	470–500	1280
Fe_2O_3	1250	1500
PbO_2	290	640
$K_2Mn_2O_8$	160	1400
K_2CrO_7	500	1500
$PbCrO_4$	600	1150
KNO_3	400	950
$NaNO_3$	380	725
$FeCO_3$	470	880
$SrCO_3$	1075	1340
$MgCO_3$	350	900
$ZnCO_3$	150–175	300
FeS	480	above 1400
CuS	220	550 (?)
FeAsS	220	

Another case of non-homogeneous system, where the solid breaks down into *two* gases is solid ammonium sulphydrate, viz.:

$$NH_4HS \text{ (solid)} \rightleftarrows NH_3 \text{(gaseous)} + H_2S \text{ (gaseous)}.$$

At 25°.1 the gaseous pressure here is equal to 501 mms., i.e., since the partial pressures of the H_2S and NH_3 are the same they are each equal to nearly 250.5 mms. of mercury. Equal only nearly, however, because this pressure includes that of the undissociated NH_4HS gas. But since this is very small (about 1 mm.) and constant at any one temperature it may be neglected.

If p_{NH_4HS} is the partial pressure of the NH_4HS gas, and p_{NH_3} and p_{H_2S} are those of the NH_3 and H_2S, then

$$(K_p p_{NH_4HS}) = \text{constant}_p = p_{NH_3} p_{H_2} .$$

The total pressure, $p = 501$ mms., is equal, by Dalton's law, to the sum of the partial pressures, and neglecting that of p_{NH_4HS}, we have,

$$p = p_{NH_3} + p_{H_2S}$$

or

$$\frac{p}{2} = p_{NH_3} = p_{H_2S},$$

and

$$\text{constant}_p = \frac{p}{2}\frac{p}{2} = \frac{p^2}{4}$$

or

$$\text{constant}_p = \frac{p^2}{4} = \frac{(501)^2}{4} = 62750.$$

This value of the " constant " may be verified experimentally by observing the effect of the addition to the dissociating system of one of the products of the dissociation, since the product of the partial pressures must always remain constant for constant temperature. In the table below are given the results of experiments carried out for this purpose, the pressures being mms. of mercury.

TABLE VII

$p_1(NH_3)$	$p_2(H_2S)$.	$p_1p_2 = \text{constant}_p$.
208	294	61152
138	458	63204
417	146	60882
453	143	64779
		Average = 62504

The average of which agrees quite well with the value previously found. In each case here a certain amount of one of the products was added before the solid is sublimed and the total pressure afterward determined. It is quite simple then to find the amount of solid which has dissociated and thus the total amount of each gas present.

Magnussen (Jour. Phys. Chem., 11, 21, 1907) who has also studied this equilibrium finds the dissociation pressure at 20° to be 355.1 mm. This gives constant $= p_{NH_3} p_{H_2S}$, a value of 3152, which holds constant for varying amounts of NH_3 and H_2S. He encountered experimental difficulties due to the adsorption of NH_3 on the solid formed, but when allowance was made for this, satisfactory agreements were observed.

The still more complicated case of the dissociation of ammonium carbamate, which does not exist as a gas, is quite similar. We have (Horstmann, Lieb. Ann., 187, 48, 1877)

$$\mathrm{NH_4OCONH_2\ (solid)} \rightleftarrows 2NH_3 + CO_2;$$

i.e.,

$$\text{constant}_p = p^2_{NH_3} p_{CO_2}.$$

But since we have 2 moles of NH_3 and 1 of H_2S, $\frac{2}{3}$ of the pressure must be due to NH_3, and $\frac{1}{3}$ to H_2S, we have then, if p is the total pressure,

$$p_{NH_3} = \tfrac{2}{3}p, \quad p_{H_2S} = \tfrac{1}{3}p;$$

hence

$$\text{constant}_p = \frac{4p^3}{27}.$$

The pressure produced by ammonium carbamate when heated to various temperatures is given below:

Temperature.	Gaseous Pressure.	Temperature.	Gaseous Pressure.
−15°	2.6 mm.	24°	84.8 mm.
− 5	7.5	30	124
0	12.4	40	248
2	15.7	48	402
4	19.0	50	470
10	29.8	55	600
18	33.7	60	770

Isambert has proven this relation to hold also when NH_3 or CO_2 are added to the system, i.e., he found that this constant holds constant just as we have seen the similar constant of the law of mass action to hold. He also showed that the presence of an indifferent gas does not affect the dissociation, for unless the volume is changed, the partial pressures would remain the same even after another gas were added. Contrary to the case of a homogeneous equilibrium an increase in volume here has no effect upon the degree of dissociation, for the solid is always completely dissociated, and reduced pressure simply causes more of the gaseous body to be produced in the same proportions as before.

For further illustrations of the application of the law of mass action to gaseous equilibrium see Jellinek, Physikalische Chemie d. Gasreaktionen, Leipzig, 1913; Haber, Thermodynamics of Technical Gas Reactions (Lamb), New York, 1908; Sackur Thermochemie und Thermodynamik, Berlin, 1912, and von Juptner, Das chemische Gleichgewicht, Leipzig, 1910.

Equilibrium in homogeneous liquid systems. — The application of the law of mass action in liquid systems is still simpler than in the case of non-homogeneous gaseous systems, for the final volume of the system does not change during the chemical reaction. The reaction

$$CH_3COOH + C_2H_5OH \rightleftarrows CH_3COOC_2H_5 + H_2O,$$

as already observed, reaches the state of equilibrium when we have present 1/3 mole acid+1/3 mole alcohol+2/3 mole ester+2/3 mole water, provided we start with 1 mole of each of the two constituents (either acid and alcohol, or ester and water).

This reaction goes very slowly at ordinary temperatures, but when it reaches the above final state it remains in it indefinitely. If we designate by v the volume of the system in liters, and start with 1 mole of acid, m moles of alcohol, and n moles of ester (or water), then in the state of equilibrium, after x moles of alcohol have been decomposed, we shall have

$$c_{\text{alcohol}} = \frac{m-x}{v}; \quad c_{\text{acid}} = \frac{1-x}{v}; \quad c_{\text{ester}} = \frac{n+x}{v} \text{ or } \left(\frac{x}{v}\right);$$

$$c_{\text{water}} = \frac{x}{v} \text{ or } \left(\frac{n+x}{v}\right) \text{ moles per liter;}$$

hence, applying the law of mass action, we obtain

$$K_c = \frac{c_{\text{ester}}\, c_{\text{water}}}{c_{\text{acid}}\, c_{\text{alcohol}}} = \frac{(n+x)x}{(1-x)(m-x)}.$$

In the special case of equilibrium above, however, $m=1$, $n=0$, $x=2/3$; hence

$$K_c = \frac{(2/3)^2}{1/3 \times 1/3} = 4.$$

This value of K_c is one of the few which are practically independent of temperature. At 10° it is found that 65.2% undergoes change, while at 220° the decomposition is but 66.5%.

This equation has been tested by experiment with very satisfactory results. *It has been found, also, as would be expected, that by using a large amount of acetic acid to a small amount of alcohol, or vice versa, the formation of ester and water is almost complete.* In the same way a large amount of water upon a small quantity of ester causes the latter to be almost entirely transformed.

In the following table some of the experimental results for this reaction are compared with the values calculated by aid of the above formula, and will serve to show how accurate this law is in its application to liquid systems.

Moles of Alcohol to 1 Mole of Acid.	Moles of Ester or Water.	
	Obs.	Calc.
0.05	0.05	0.049
0.08	0.078	0.078
0.18	0.171	0.171
0.28	0.226	0.232
0.33	0.293	0.311
0.50	0.414	0.423
0.67	0.519	0.528
1.00	0.665	0.667
1.50	0.819	0.785
2.00	0.858	0.845
2.24	0.876	0.864
8.00	0.966	0.945

Using 1 mole of acid, 1 mole of alcohol, and various amounts of water (no ester being added) we find the following results:

Moles of H_2O to 1 Mole of Acid + 1 Mole of Alcohol.	Moles of Ester Formed.	
	Obs.	Calc.
0	0.665	0.667
0.5	0.614	0.596
1.0	0.547	0.542
1.5	0.486	0.500
2.0	0.458	0.465
4.0	0.341	0.368
6.5	0.284	0.288
7.5	0.198	0.212

Amylene in contact with acid forms an ester, according to the equation

$$CH_3COOH + C_5H_{10} \rightleftarrows CH_3COO(C_5H_{11}).$$

If x is the amount of ester formed when equilibrium is established, v is the volume of the system, and 1 mole of acid and a moles of amylene are present originally, then $\frac{a-x}{v}$ = amount of amylene left; $\frac{1-x}{v}$ = amount of acid left; $\frac{x}{v}$ = amount of ester formed; hence

$$K_c = \frac{C_{\text{ester}}}{C_{\text{amylene}}C_{\text{acid}}} = \frac{xv}{(a-x)(1-x)}.$$

As will be observed, the volume here, since there are not the same number of formula weights on both sides, must be retained in the formula. The value for K_c in this case has also been determined experimentally. It was found that

$$K_c = \frac{1}{.001205},$$

the constant in the form $K_c' = \frac{(a-x)(1-x)}{xv}$, having the value 0.001205.

The agreement of theory and experiment in this case, the acid being trichloracetic, is shown by the following summary:

a.	v (liters).	x obs.	x calc.
2.15	361	0.762	0.762
4.12	595	0.814	0.821
4.48	638	0.820	0.826
6.63	894	0.838	0.844
6.80	915	0.839	0.845
7.13	954	0.855	0.846
7.67	1018	0.855	0.846
9.12	1190	0.857	0.853
9.51	1237	0.863	0.853
14.15	1787	0.873	0.861

Non-homogeneous liquid systems. The coefficient of partition or distribution.—The simplest case of the non-homogeneous system of solid and liquid is where a solid substance is present in excess with its saturated solution, when we find that the concentration of the substance is constant for any one temperature. We have then simply just as with liquid and its vapor, $\text{constant}_c = c$, where c is the number of moles per liter of un-ionized or very slightly ionized substance in solution, and can be treated just as K_c, in the van't Hoff equation for example.

In case we dissolve a substance in a system of two immiscible liquids, the substance being soluble in both liquids, we find under definite conditions, a so-called coefficient of partition or distribution of the substance between the two liquids. In other words, the ratio of the concentrations of the substance in the unit of volume of the two solvents, under these conditions, is a constant, independent of the amount of substance with which we start.

Let the relation, in general, of a substance in two solvents be

$$A_N \rightleftarrows NA,$$

i.e., let us assume that the molecular weight of the dissolved substance is N times as great in the one solvent as it is in the other. Applying our criterion of equilibrium here, we find,

$$K_c = \frac{c_A{}^N}{c_{A_N}}$$

The ratio of the concentration of substance in the one solvent, raised to a power equal to the number of moles which are produced in that solvent by the loss of 1 mole of the substance from the other, to the concentration of substance in the other solvent, is a constant, at any one temperature.

It is possible to simplify this equation somewhat by the substitution of grams of substance per unit of volume (1 liter or 100 cc. or 1 cc., etc.), in place of moles. Since

$c_A = \frac{w_A}{M_A}$, and $c_{A_N} = \frac{w_{A_N}}{M_{A_N}}$, the above equation then becomes

$$K_c = \left(\frac{w_A}{M_A}\right)^N \Big/ \frac{w_{A_N}}{M_{A_N}}$$

or

$$\text{constant} = \left(\frac{M_A{}^N}{M_{A_N}} K_c\right) = \frac{w_A{}^N}{w_{A_N}}.$$

When the formula weight in the one solvent is always N times that in the other (at the dilutions considered), the coefficient of distribution in the form $\frac{w_A{}^N}{w_{A_N}}$ *(the terms w being the grams per unit of volume of solvent) will remain constant, independent of the original dilution.*

If the coefficient of distribution in the form $\frac{w_1}{w_2}$ (the subnumerals indicating the solvent) *is constant at all dilutions of the original solution in the one solvent, then, the molecular weight of the distributing substance must be identical in the two solvents,* i.e., N above must equal 1. In connection with the possible errors in this method, see Bancroft, J. Phys. Chem., **12**, 30–35, 1908.

If the formula weight in solvent (2) is twice that in solvent (1), then it is obvious that $\frac{w_1{}^2}{w_2} = \text{constant}$, or $\frac{w_1}{\sqrt{w_2}} = \text{Constant}$, at all dilutions. An illustration of this is given by the distribution of benzoic acid between water (1) and benzene (2), the values being 0.062, 0.0408, and 0.030 for $\frac{w_1}{w_2}$, while those of $\frac{w_1}{\sqrt{w_2}}$, for the same total dilutions, are 0.0305, 0.0304 and

0.0293. Benzoic acid, therefore, has by this method a molecular weight which is twice as great in benzene as in water, a fact which is also shown by the freezing-point method, using first water and then benzene as the solvents.

The coefficient of distribution is an exceedingly important method for three purposes: *First*, it gives us an additional method (a relative one here) for the determination of the molecular weight of a substance in solution in the one solvent, where it is known in another solvent which is immiscible with the first. In this way we can find molecular weights of substances in solvents where the other methods (Chapter V) would not apply. Thus by this method it has been proven that the molecular weight of ethyl alcohol in ether is identical with what it is in water, and in the gaseous state, which could not have been done by either the boiling-point method, or that depending upon the change in vapor pressure (for both solute and solvent are volatile), and which would give but uncertain results by osmotic pressure, or by the freezing-point method at the very low freezing-point of ether.

Second, the coefficient of distribution is a very valuable method for the ascertaining of the amount of any one substance in an equilibrium in the one solvent, when the other solvent is so selected that in addition to being immiscible with the first, it only dissolves out that one constituent. Naturally, here, since we remove one constituent of the equilibrium from the solvent, the reaction progresses to form a new state, but giving of course the same value of the criterion of equilibrium, so that from the amount left in that solvent, which can be found from the coefficient and that in the other solvent, and the chemical reaction taking place to produce the new equilibrium state, we can calculate the value of K_c for the reaction. An example of this is given later (under hydrolytic dissociation) which shows how the amounts of all the constituents in the equilibrium can thus be calculated.

Third, the coefficient of distribution enables us to extract with the greatest efficiency, any substance from solution in one solvent by treatment with another, immiscible, solvent, in which the substance is also soluble. The net result of the application of the distribution law here, as will be seen below, is that the *successive treatment of a volume of solvent containing a dissolved substance, with a number of* FRACTIONAL *parts of the new solvent, causes the removal of more substance than is possible by application of the same total amount of the new solvent used at one time.*

Since each solvent probably dissolves some of the other, the solubility phenomena of the two layers of liquid considered alone would be somewhat different, in general, from those of the pure liquids. Naturally, also, if the substance is difficultly soluble in one solvent, and the amount available for distribution is large, it is conceivable that the amount found per unit of volume of the second solvent would always be constant; in other words it would always form a saturated solution in that solvent. In such a case the law of distribution would only hold for such small amounts of substance in total as to lead to an unsaturated solution in the other solvent, if it were considered by itself.

In case we are to determine the molecular weight of a substance in solvent (1), when we know it in solvent (2),—we would first establish equilibrium for a number of concentrations of solution in solvent (2), treating the solution with an equal volume of the solvent (1) in each case, and analyze both layers in each system for the number of grams of substance per unit of volume of solvent. Calling these amounts, for three treatments, for example, w_1', w_1'', w_1''' and w_2', w_2'', w_2''', where w_1' and w_2', etc., are found at equilibrium in the same system, we can write

$$\frac{w_1'^{N}}{w_2'} = \frac{w_1''^{N}}{w_2''} = \frac{w_1'''^{N}}{w_2'''} = \text{constant};$$

from which, using the ratios in pairs, we could calculate the value of N. If N is larger than unity, then, it would indicate that the molecular weight in (2) is N times that in solvent (1)—if N is fractional, on the other hand, it would mean that the molecular weight in (1) is N times that in (2).

An illustration of the use of the method to find the amount of a substance present in equilibrium with other substances in a solvent is as follows: The coefficient of distribution of iodine between carbon disulphide and water is

$$\text{constant} = \frac{w_{CS_2}}{w_{H_2O}} = 410,$$

at a certain temperature. After extracting the iodine present in a more or less complicated equilibrium in water with an equal volume of CS_2, it is found that there are 35.42 grams of I per liter left in the CS_2 layer. The present amount in the water, per liter (the equilibrium having been displaced, naturally), is therefore x in

$$\frac{35.42}{x} = 410; \quad x = 0.0864 \text{ gram of free I.}$$

From this value, knowing the nature of the equilibrium in water, and the amount lost to the CS_2, we could now readily calculate the present, coexisting, amounts of the various constituents of the equilibrium in the water—since it is only the iodine which has distributed.

To see how successive treatments with small amounts of the new solvent extracts more substance from the other than could be extracted by the same total volume of the extracting solvent used at one time, let us consider the following system: The substance D distributes between the two immiscible solvents *A* and *B* (the molecular weight of *D* being identical in both) so that at equilibrium we have

$$\text{constant} = \frac{w_B}{w_A} = 0.05,$$

which means that at equilibrium there is always 20 times as much *D* in the solvent *A*, as there is in an equal volume of the solvent *B*.

If we start now with 1 liter of *B*, containing 3.51 grams of *D*, and mix the solution with 1 liter of *A*, and at equilibrium assume x grams of *D* to still remain in the liter of *B*, we must have lost $(3.51-x)$ grams of *D* from the liter of *B* to the liter of *A*. We would have then

$$\frac{x}{3.51-x} = 0.05; \quad x = 0.1671 \text{ gram}.$$

By the one extraction from the 1 liter of *B* with 1 liter of *A*, then, we have removed *D* down to 0.1671 gram per liter.

Let us now see how much *D* could be removed from 1 liter of *B* by 1 liter of *A*, applied, not at once, but in five equal, successive, portions of 200 cc. each. If the amount left in the liter of *B* after treatment with the first 200 cc. of *A* is a grams, we must have lost $(3.51-a)$ grams from the liter of *B* to the 200 cc. of *A*, which would be $5(3.51-a)$ grams per liter of *A*. We can write then

$$\frac{a}{5(3.51-a)} = 0.05; \quad a = 0.702.$$

Removing this 200 cc. of *A* from the system, by aid of a separatory funnel, and substituting for it 200 cc. of pure *A*, knowing that in the liter of *B* we now have but 0.702 gram of D, we find, if b is the number of grams of D left in B after this extraction,

$$\frac{b}{5(0.702-b)}=0.05; \quad b=0.1402.$$

Continuing in this way with the other three portions successively, if c, d and e are the amounts left in B, we have $\frac{c}{5(0.1402-c)}=0.05$; $c=0.02807$; $\frac{d}{5(0.02807-d)}=0.05$; $d=0.005614$; $\frac{e}{5(0.005614-e)}=0.05$; $e=0.001123$. In total, then, by the five successive treatments of the original 1 liter of B containing 3.51 grams of D, with 200 cc. of A each time, we remove all but 0.001123 gram of it; where the one treatment with the liter of A at one time left 0.1671 gram.*

It will be seen that this method, which could give even better results under other conditions, is especially important for the separation of a substance from a mixture of others (for the coefficient of distribution of a substance between two solvents is independent of the presence of other substances), for various substances could thus be removed, one at a time, by the proper selection of a second solvent which would dissolve out only the desired substance.

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* Starting with 1 liter of B containing a grams of substance, and using successively n portions of b cc. each of A, it can be shown readily that after the nth extraction we would have left in the liter of B, $x_n=a\left(\frac{\frac{1000}{b}K}{1+\frac{1000}{b}K}\right)^n$, where K is the coefficient of distribution 1, i.e., is equal to $\frac{w_B}{w_A}$. In this way, in the above case, we would find after the fifth extraction, $x_6=3.51\left(\frac{5\times 0.05}{1+5\times 0.05}\right)^5$, from which we find $x=0.0001123$ just as above.

An interesting modification of this law has been suggested by Herz and Kurzer and by Herz (Z. f. Elektrochem., 16, 240, 1910; Nernst's Festschrift, Halle, 1912, pp. 190–5), who employ as one of the solvents two liquids miscible with one another, but immiscible with the third one—the mixed solvents of course also dissolving the distributing substance. The valuable idea in this, perhaps, is the possibility it offers for the study of the properties of mixed liquids as dependent upon their relative amounts in the mixture—for if a chemical compound were formed from the two liquids at any special mixture-ratio, we would expect a sudden change in the solubility proportions. In many cases studied, the mixed liquids behave just as a single one would, and exhibit no sharp change for changed proportions of mixture.

For illustrations of the above law, see Nernst, Zeit. f. phys. Chem., 8, 110, 1891; Aulich, *ibid.*, 8, 105, 1891; Hantzsh and Sebalt, *ibid.*, 30, 268, 1896; Hantzsh and Vagt, ibid., 38, 705, 1901; Morse, Zeit. f. phys. Chem., 41, 722, 1902; Herz and Fischer, Ber., 38, 1138, 1905; Herz and Lewy, Zeit. f. Elektrochem., 11, 818, 1905; Dawson, Trans. Chem. Soc., 89/90, 1666–1674, 1906; Morgan and Benson, Jour. Am. Chem. Soc., 29, 1176–1179, 1907; Marden, Jour. Ind. and Eng. Chem. 6, 315-20, 1914, and others.

B. Chemical Kinetics

Application of the law of mass action.—Thus far we have considered only the equilibrium which is attained *after* the reaction has come to rest, i.e., after the two sides bear a constant relation to one another. The question now arises as to the progress of a reaction toward this state, and the factors upon which the time necessary to attain it depends.

By aid of the law of mass action, it is possible to find an answer to both portions of this question. Since chemical action at any time, according to it (p. 251), is proportional, for constant temperature, to the active masses of the substances present, i.e., to those portions which are free to act, we find, when we have two substances reacting, the concentrations being a_1 and a_2 moles per liter,

$$\frac{dx}{dt}=k(a_1-x)(a_2-x),$$

where x is the fraction of a mole of each which decomposes in the time t. The term k in this equation is known as the *velocity coefficient* of the reaction, and is constant, at any one temperature, for any value of x in the reaction in question.

Suppose we have the reversible reaction

$$A_1+A_2 \rightleftarrows A_1'+A_2',$$

which after a time attains a state of equilibrium in which all four products are present. The relative amounts of these at equilibrium are dependent upon the value of K_c for the reaction at this temperature, according to the relation

$$K_c=\frac{c_1'c_2'}{c_1c_2}.$$

If we start with a_1 moles of A_1 and a_2 moles of A_2, then, the rate of transformation of A_1 and A_2 into A_1' and A_2' will be

$$\frac{dx}{dt}=k(a_1-x)(a_2-x).$$

But if we start with a_1' moles of A_1' and a_2' of A_2', the rate of the transformation of A_1' and A_2' into A_1 and A_2 will be

$$\frac{dx'}{dt}=k'(a_1'-x')(a_2'-x'),$$

where $\frac{dx'}{dt}$ is the velocity in the opposite direction.

Starting with the substances on either side, then, those on the other will exert an ever-increasing influence upon the velocity due to the initial substances, and this velocity must decrease continually. Finally, however, equilibrium (the common limit of the two inverse reactions) will be attained, and the ratio of the amounts on the two sides will remain constant, i.e., the reaction as a whole ceases, and any motion which exists is so compensated by the contrary one that no lasting change results.

Imagine now we start with a_1 moles of A_1 and a_2 moles of A_2. The total velocity due to these at any one time, during the progress of the reaction, will be, then,

$$\frac{dX}{dt}=\frac{dx}{dt}-\frac{dx'}{dt}=k(a_1-x)(a_2-x)-k'(x)(x),$$

and at equilibrium, i.e., where $\frac{dX}{dt}=0$, we would have

$$k(a_1-x)(a_2-x)=k'x^2,$$

or

$$\frac{k}{k'}=K_c=\frac{x^2}{(a_1-x)(a_2-x)},$$

i.e., *the equilibrium constant, K_c, of any reversible reaction is equal to the velocity coefficient of that reaction to the right, divided by the velocity coefficient to the left.*

This has been proven to be true for a number of cases. Thus for the system acid-alcohol (p. 287) it was found for a certain strength acid that $k=0.000238$ and $k'=0.000815$, from which $K_c=\frac{k}{k'}=2.92$, while direct experiment gave $K_c=2.84$.

All this is true, however, only when the reaction takes place isothermally, i.e., when the heat liberated or absorbed is removed *or added, and no change in the temperature results; for the numerical values of the speed constants k and k′ are very dependent upon the temperature.*

In general the application of this formula is very much simplified by the fact that many reactions are almost complete in one direction, so that the second term will be so small that it may be neglected. We have then

$$\frac{dx}{dt}=k(a_1-x)(a_2-x).$$

In all these cases the values on the right are obtained by subtracting the loss from the concentration of the original substance and having as many such terms as there are moles in the formula. Thus for the reaction $AB_2 \rightleftarrows A+2B$ we would write

$$\frac{dx}{dt}=k(c_B-x)(c_B-x)(c_A-x).$$

This is simply custom, for we could also write it

$$\frac{dx_1}{dt}=k_1(c_B-2x)^2(c_A-x),$$

and the k value would still be constant, but the later integration of the expression would be more difficult.

Reactions of the first order.—For convenience we shall divide all reactions into orders. Thus a reaction of the first order is one in which but one mole of substance suffers a change in concentration.

Cane-sugar in water solution is transformed in the presence of acids almost completely into dextrose and lævulose; i.e., it is inverted. The speed of the reaction is very low and increases with the amount of acid added.

The progress of this reaction may be observed by aid of the polariscope. The uninverted portion revolves the plane of polarization to the right, while the two products revolve it to the left. If α_0 is the positive angle of revolution at the time $t=0$, i.e., is that which is due to the uninverted sugar alone, the amount of which is a moles, α_0' is the negative angle after complete inversion, and α is the angle at the time t, then, since the revolution is proportional to the concentrations, x, the amount inverted, is found from

$$x=a\frac{\alpha_0-\alpha}{\alpha_0+\alpha_0'}.$$

For the time $t=0^\circ$, $\alpha=\alpha_0$, i.e., $x=0$; for the time $t=\infty$, i.e., after complete inversion, $\alpha=-\alpha_0'$ or $x=a$.

This reaction was first studied by Wilhelmy (1850), and it has played an important rôle in the history of chemical mechanics.

The process follows the scheme

$$C_{12}H_{22}O_{11}+H_2O \rightleftarrows 2C_6H_{12}O_6,$$

whether acid is used or not, for the concentration of the latter does not change during the reaction. According to the law of mass action, the speed is proportional to the amounts of sugar and water. The latter, however, is present in such an excess that its action may be regarded as constant. The speed of reaction, then, is really proportional to the amount of sugar present and we have a reaction of the first order, i.e., the formula is

$$\frac{dx}{dt}=k(a-x),$$

where, for $t=0$, $x=0$, and k is called the *inversion coefficient*, which depends only upon the temperature. By integration this becomes

$$-\log_e(a-x)=kt+\text{constant},$$

or since, for $t=0$, $x=0$,

$$-\log_e(a)=\text{the constant},$$

i.e.,

$$k=\frac{1}{t}\log_e\frac{a}{a-x}=\frac{1}{t}\log_e\frac{\alpha_0+\alpha_0'}{\alpha+\alpha_0'};$$

in other words, a constant fraction of the total amount of sugar is inverted in each unit of time.

The meaning of the constant k in words is as follows: *Its reciprocal value multiplied by the natural logarithm of 2 gives the time in minutes which is necessary for the transformation of one-half the total amount of substance, provided the products of the reaction are removed as soon as they are formed, and the substances replaced as they are used.* This is shown by the substitution of $\frac{a}{2}$ for x. Further, for all reactions of the first order, *this constant k is independent of the original concentration of the substance.* The table below gives the values for k for a 20% sugar solution in presence of a 0.5 N solution of lactic acid at 25° C., k being given in terms of logarithms to the base 10, since it is only the constancy of the term that is to be shown.

INVERSION OF SUGAR [1]

t (minutes).	α.	$\frac{1}{t}\log_{10}\frac{a}{a-x}$.
0	34°.5	......
1435	31°.1	0.2348
4315	25°.0	0.2359
7070	20°.16	0.2343
11360	13°.98	0.2310
14170	10°.61	0.2301
16935	7°.57	0.2316
19815	5°.08	0.2291
29925	− 1°.65	0.2330
∞	−10°.77	......

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[1] $\alpha_0=34.5$; $\alpha_0'=-10.77$. $\alpha_0+\alpha_0'=45.27$.

Catalytic action of hydrogen ion. Catalysis. — The inversion of sugar, as well as all other reactions of the first order which are hastened by the action of acids, is apparently due to the ionized hydrogen which is present. This action is known as a catalytic action of the acid present, which retains throughout the reaction its original concentration. The reason why H^+ ion should act in this way is unknown; but that it does have an accelerating effect is an established fact.*

In general a catalytic reagent is one that hastens the reaction in which it is without at the same time having its concentration changed by the reaction; and also without changing in any way the final equilibrium state, though it does cause this to be attained more rapidly.

An example of such an action is given by the increased speed of solution of metallic mercury, silver, or copper in a nitric-acid solution in which one of these has already been dissolved to a slight extent. The catalytic action here is due to the formation of the oxides of nitrogen, for these, when passed into the nitric acid from an exterior source, cause the same action as the above.

Since the catalyser takes no part in the reaction it does not alter the equilibrium constant, hence it must also hasten the reverse action, so that $\frac{k}{k'}$ may remain constant, and be equal to K_c at equilibrium. As there is no general law known for catalytic action the reader must be referred elsewhere for the vast number of isolated facts.

The more concentrated the acid used, the more rapidly the sugar is inverted, without, however, any exact proportionality. The inverting action increases more rapidly than the concentration. In presence of a neutral salt of the acid its inverting power is increased by about 10% for the stronger acids, but decreased for the weaker ones.

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* See Bredig, Biochem.Zeit.,6,283, 1907, and Sorensen, *ibid.*, for 1909 and later. For an interesting connection between the catalytic power of an acid and its un-ionized portion, see Taylor, Zeit. f. Elektrochem., 20, 201–204, 1914.

Since the acceleration of the speed of the reaction is caused only by acids, and since they are distinguished by the presence of H^+ ion, the catalytic effect must be due to this. Further than this, a series of acids arranged in the order of inverting power is found to be in the same order in which they stand in reference to ionization. Thus it is plain that H^+ ion has this effect, although in *concentrated* solutions the inverting power is not strictly proportional to the ionization. For example, a 0.5 N solution of HCl inverts 6.07 times as rapidly as a 0.1 N solution, while it contains only 4.64 times as much ionic H^+. Arrhenius found that the presence of other ions tends to increase the catalytic action of H^+.

That the speed of reaction increases more rapidly than the concentration of H^+ ion is assumed to be due to the fact that the negative ions, present to an equal amount, also increase the inverting action of H^+ ion.

In the presence of a neutral salt, then, we have two separate actions upon the acid; the first causes a decrease in the concentration of H^+ ion of the acid; the second accelerates the action of the H^+ ion left.

The stronger acids are less influenced by the former than the weaker ones, because they are ionized more nearly to the extent to which their salts are. Consequently the second action predominates, and we have the greatest inverting power for the strong acids when a salt is present.

For the weaker acids, however, the second action is the smaller; hence the inverting action is less for weak acids in presence of a salt.

Palmaer has found in dilute solutions, when the influence of the neutral-salt action is avoided, that the inversion constant is exactly proportional to the concentration of hydrogen ion.

Another reaction of the first order which depends for its speed upon the catalytic action of H^+ ion is the formation of alcohol and acid from an ester. For example,

$$CH_3COOC_2H_5 + H_2O \rightleftarrows CH_3COOH + C_2H_5OH.$$

The equation for the speed of this reaction is the same as that given above, i.e., it also follows the law of a first order reaction, viz.,

$$k = \frac{1}{t} \log_e \frac{a}{a-x},$$

where a is the amount of ester in moles at the time $t=0$ (at the start), and x is the amount transformed at the time t, and is equal also to the amount of acid or alcohol formed by the reaction during the time t. The progress of this reaction is observed by titrating the amount of free acetic acid present.

Ostwald measured the value for the reaction with methylacetate. He started with 1 cc. of methylacetate and 10 cc. HCl (1 mole to the liter), diluted to 15 cc. To neutralize this acid 13.33 cc. of a $Ba(OH)_2$ solution would be necessary. The amounts of acetic acid formed are shown by titration, after subtracting 13.33; these amounts, expressed in cc. of $Ba(OH)_2$ solution, for various times are as follows:

0	14	34	199	539	∞	Minutes.
—	0.92	2.14	8.82	13.09	14.11	cc.

The amount of ester (a) is represented, then, by 14.11, $a-x$ being this value minus 0.92, 2.14, etc. The values thus determined for k are 0.00209, 0.00210, 0.00214, and 0.00212.

Another reaction which gives a constant when considered as a reaction of the first order is the one which is usually written

$$4AsH_3 = As_4 + 6H_2.$$

Since at 310° this fulfils the definition of a reaction of the first order, it should be written not as above, as of the fourth order, but as of the first, i.e.,

$$AsH_3 = As + 1\tfrac{1}{2}(H_2).$$

In the case of the above ester reaction, also, the velocity is exactly proportional when the action of the neutral salt is avoided. If the amount of neutral salt in the solution is so large that it can be considered constant, then a constant value will be obtained for k, although its absolute value will be different from that for the case that no neutral salt is present. Walker used this method to determine the concentration of H^+ ion present in a solution due to hydrolytic dissociation, which we shall discuss in detail below; while Bredig and Fraenkel (Z. f. Elektrochem., 11, 525–529, 1905) advocate for this purpose diazoacetic ester as a very accurate means to estimating concentrations of H^+ ion of $n/1000$ and less. (See also Sorensen, Biochem. Zeit. for 1909 and later, and Baccarini, Nuovo Cimento, 6, 286–290.)

Reactions of the second order.—Here two moles of substance suffer a change in concentration during the reaction, i.e., the constant depends upon the concentration of two substances. We have then

$$\frac{dx}{dt} = k(a-x)(b-x),$$

or

$$-\frac{1}{a-b}[\log_e(b-x) - \log_e(a-x)] = kt + \text{constant}.$$

For $t=0$, $x=0$, and the constant is

$$-\frac{1}{a-b}(\log_e b - \log_e a);$$

i.e.,

$$k = \frac{1}{(a-b)t} \log_e \frac{(a-x)b}{(b-x)a}.$$

If we use equivalent amounts of the two substances here, then $a=b$, and we have

$$\frac{dx}{dt}=k(a-x)^2,$$

or

$$k=\frac{1}{t}\frac{x}{(a-x)a}.$$

Here k is inversely proportional to the original concentration.

An example of a reaction of the second order is

$$CH_3COOC_2H_5+NaOH \rightleftarrows CH_3COONa+C_2H_5OH.$$

The table below gives the value of this constant as calculated for different lengths of time at the temperature of 10° C.:

t (minutes).	Amount NaOH in cc. of Acid.	k.
0	61.95	....
489	50.59	2.36
1037	42.40	2.38
2818	29.35	2.33
∞	14.92	....

The question as to how the speed varies with the nature of the base used has been investigated quite thoroughly. Thus Reicher (Lieb. Ann., 128, 257, 1885) and Ostwald (J. pr. Chem., 35, 112, 1887) found for strong bases (those which are largely ionized) approximately equal values for k; for weak ones, however, very much smaller values were found. Ostwald observed that the weak bases ammonia and allylamine fail to give a constant value for k. Thus for ethyl acetate and ammonia he found the following values:

t (minutes).	k.
0	.....
60	1.64
240	1.04
1470	0.484

This failure to give a constant he recognized, however, as being due to the effect of the neutral salt formed (ammonium acetate) upon the weak base. When a large amount of this is present a constant is obtained, as is shown by the following table:

t (minutes).	k.
0	.....
994	0.138
6874	0.120
15404	0.119

This shows still a slight effect of the neutral salt formed, for it is impossible to keep it perfectly constant.

Arrhenius found that the base acts simply in proportion to the amount of ionized OH^- it contains, i.e., we have

$$C_2H_3O_2C_2H_5+OH^-+Na^+ \rightleftarrows C_2H_3O_2^-+Na^++C_2H_5OH.$$

According to this, all bases containing the same amount of OH^- ion should give the same constant. We can rearrange our equation, then, in the form

$$\frac{dx}{dt}=k'\alpha(a-x)(b-x),$$

where α is the degree of ionization of the base. Since the strong bases are but slightly influenced by the addition of salts with an ion in common, the constant of KOH can be taken, with very little error, to be that due to a certain concentration of OH^- ion. From this it is then possible to calculate the constant for NH_4OH, with or without an ammonium salt present. A N/40 solution of KOH at 24°.7 C. gives a constant equal to 6.41. Such a solution of NH_4OH is but 2.69% ionized, while the ionization of that of KOH is 97.2%. The constant, then, for NH_4OH in the absence of salt is

$$k_{NH_4OH} : k_{KOH} :: 0.0269 : 0.972,$$

or

$$k_{NH_4OH} = \frac{0.0269}{0.972} 6.41 = 0.177.$$

The effect of the neutral salt upon the NH_4OH can be readily calculated from the ionization of the two; we have, then, the constant for NH_4OH in presence of a neutral salt,

$$k'_{NH_4OH} = \frac{\alpha}{0.972} 6.41,$$

where α is the concentration of OH^- ion in the NH_4OH in presence of the amount of the neutral salts, the concentration of which is designated below by s. The following table compares the values thus obtained with those actually observed by experiment.

SPEED OF REACTION CAUSED BY NH_4OH

s.	a.	k (calculated).	k (observed).
0	2.69%	0.177	0.156
0.00125	1.21	0.08	0.062
0.005	0.71	0.047	0.039
0.0175	0.118	0.0078	0.0081
0.025	0.082	0.0054	0.0062
0.05	0.042	0.0028	0.0033

This is a very good agreement, considering the possible experimental errors, so that we may conclude that *the velocity of saponification is proportional to the concentration of* OH^- *ion present, and is independent of the radical by which it is accompanied.*[*]

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[*] For another method for the determination of OH^- ion concentrations see Francis and Gaeke, Trans. Chem. Soc., 101, 2358, and **103**, 1722.

In a second order reaction the effect of either constituent upon the velocity should be the same.

Reactions of the third order.—If the three substances are present, in equimolecular amounts, i.e., if three moles change in concentration, we have

$$\frac{dx}{dt}=k(a-x)^3,$$

or

$$k=\frac{1}{t}\,\frac{x(2a-x)}{2a^2(a-x)^2}.$$

A reaction of this order has been studied by Noyes (Zeit. f. phys. Chem., 16, 546, 1895). The reaction is

$$2FeCl_3+SnCl_2=2FeCl_2+SnCl_4,$$

or

$$2Fe^{+++}+Sn^{++}=2Fe^{++}+Sn^{++++}.$$

The results, starting with a concentration of .025 mole of each, $SnCl_2$, $FeCl_3$, $SnCl_4$ and $FeCl_2$, were as follows:

Time.	x	$a-x$.	k.
2.5	0.00351	0.02149	113
3	0.00388	0.02112	107
6	0.00663	0.01837	114
11	0.00946	0.01554	116
15	0.01106	0.01394	118
18	0.01187	0.01313	117
30	0.01440	0.01060	122
60	0.01716	0.00784	122
			Average = 116

For such a reaction of the third order k is inversely proportional to the square of the original concentration; and k for a reaction of the nth order would be inversely proportional to the $(n-1)$ power of the original concentration.

In a third order reaction the effect of the addition of one constituent on the velocity should not, of course, be the same as that produced by an excess of the other; for the above, indeed, Noyes found that an excess of ferric chloride has a greater effect in hastening the reaction than one of stannous chloride has, just as we should expect from the equation.

Reactions of the fourth, fifth, and higher orders have also been investigated. Examples of the fourth order are as follows: The decomposition of $KClO_3$ at 395° which takes place according to the scheme

$$4KClO_3 = KCl + 3KClO_4$$

(Scobai, Zeit. f. phys. Chem., 44, 319, 1903); the reaction between hydrobromic and bromic acids, under certain conditions (Walker and Judson, Trans. Chem. Soc., 73, 410, 1898); the action of chromic acid upon phosphoric acid (Viard, C. r., **124**, 148, 1897); and the reaction between bromine and benzene (Bruner, Zeit. f. phys. Chem., 41, 513, 1902).

An example of a reaction of the fifth order, which has been studied by Donnan and Le Rossignol (Trans. Chem. Soc., 83, 703, 1903) is the action of potassium ferricyanide upon potassium iodide. And one of the eighth order, studied by Luther and MacDougal (Zeit. f. phys. Chem., 62, 199–243, 1908), is the action of chloric acid upon hydrochloric acid, and may be written in its ionic form as follows:

$$4H^+ + 2ClO_3^- + 2Cl^- \rightarrow 2ClO_2 + Cl_2 + 2H_2O.$$

For a different handling of the fundamental differential equations of chemical kinetics than the above, see Bray (Jour. Phys. Chem., 9, 573–587, 1905) and De Lury (*ibid.*, 10, 423–444, 1906).

Incomplete reactions.—Thus far we have considered the speed of reactions which are complete, i.e., those which cease only when all the original substance has been transformed. In the case where this is not true it is necessary to use the equation in its original form. Such a case is the one already studied,

$$C_2H_5OH + CH_3COOH \rightleftarrows CH_3COOC_2H_5 + H_2O,$$

which goes with a certain speed until two-thirds of the acid and alcohol are decomposed. When the amount of ester is equal to x, then

$$\frac{dx}{dt} = k(1-x)^2 - k'x^2,$$

where we start with 1 mole of each, acid and alcohol, and have no water or ester present, and k and k' are the velocity coefficients in the two directions, related, as was shown above to the value K, of the criterion of equilibrium by the equation

$$K = \frac{k}{k'} = 4.$$

By observing the change for any time, t, we find

$$k - k' = \frac{3}{4t} \log_e \frac{2-x}{2-3x}.$$

From these two values $\frac{k}{k'}$ and $k-k'$ we can find k. The reaction so measured, however, does not give a constant value for k. This was accounted for by Kistiakowsky (Wied. Beibl., 1891, p. 295) and Knoblauch (Z. f. phys. Chem., 22, 268, 1897). When alcohol and acetic acid form ester and water the reaction goes faster than it should, according to the theory. This is due to the catalytic action of the H^+ ion present when the reaction goes in the one direction. If, then, the concentration of H^+ ion be retained the same throughout the reaction,

k should be constant, which has been found by experiment to be the case.

This shows the importance of secondary reactions, which may lead to entirely false results unless accounted for.

Heterogeneous systems.—The solution of a substance in an acid depends for its speed upon the surface of contact between the two, and upon the strength of the acid; but many secondary reactions can take place here, so that our results are only approximate.

If we assume the surface to be so large that it changes but slightly during the reaction we may consider it as constant; we have then, if S is the surface,

$$\frac{dx}{dt} = kS(a-x),$$

where x is the amount dissolved in the time t. By integration we find

$$kS = \frac{1}{t} \log_e \frac{a}{a-x}.$$

The formula in this form was found by Boguski (Ber., 9, 1646, 1876; *ibid.*, 10, 34, 1877) to give constant results, within the experimental error, for the solution of marble in acid. Noyes and Whitney (Zeit. f. phys. Chem., 23, 689, 1897) have proved that the speed of solubility of a solid substance in any instant is proportional to the difference between the concentration of saturation and the one at the time of the experiment. Further work of this sort has been done by Bodenstein and others, see Zeit. f. phys. Chem., 60, 1–67, 1907; 53, 166, 1905; 49, 41, 1904; and 46, 725, 1903.

Speed of reaction and temperature.—Empirically it has been found that *the speed of a reaction always increases with an increase in the temperature.* The increase in many cases is very great. Thus a rise in temperature of 30° causes the speed of the inversion of sugar to become five times as great as it was before. An empirical formula from which the change in speed with the temperature can be calculated, was found by van't Hoff and tested by Arrhenius. We have

$$k_1 = k_0 e^{A(T_1 - T_0)/T_0 T_1},$$

where k_0 is the velocity coefficient at the temperature T_0, k is the constant at T_1, e is the base of the natural system of logarithms, and A is a numerical constant. Using the lower of two temperatures as T_0, we have for the transformation of ammonium cyanate into urea

$$T_0 = 273 + 25°, \quad k_0 = 0.000227, \quad A = 11700.$$

T_1	k (obs.).	k (calc.).
273+39	0.00141	0.00133
273+50.1	0.00520	0.00480
273+64.5	0.0228	0.0227
273+74.7	0.062	0.0623
273+80	0.100	0.105

Trautz and Volkmann (Zeit. phys. Chem., 64, 53–88, 1908), give a bibliography of the temperature coefficient of reaction velocity, which is complete up to that date. See also Goldschmidt, Dissertation, Breslau, 1907.

C. APPLICATION OF THE LAW OF MASS ACTION TO ELECTROLYTES—IONIC EQUILIBRIA

Organic acids and bases. The Ostwald dilution law.—The application of the law of mass action to gaseous equilibria, as well as to those existing in solutions of non-electrolytes—in short to chemical equilibria—has shown that it is a general law of nature, holding between very wide limits. The question which naturally arises here, then, is, Can the law of mass action also be applied to those equilibria existing between the ionized and unionized portions of a substance in solution? In other words, Is the law of mass action the principle governing the amounts of these portions which can exist together in equilibrium? It is the purpose of this section to answer this question so far as it is possible from our present knowledge of the facts.

The conductivity ratios $\frac{\Lambda_{v_e}}{\Lambda_\infty}$, as well as the methods for determining the average molecular weight, where these can be carried out with sufficient accuracy, show that a water solution of acetic acid is ionized according to the following scheme:

$$CH_3COOH \rightleftarrows CH_3COO^- + H^+.$$

From this equation, applying the law of mass-action, we obtain

$$K_c = \frac{c_{CH_3COO^-} \times c_{H^+}}{c_{CH_3COOH}};$$

or, in the presence of a moles of H^+ ion from another acid added to the system.

$$K_c = \frac{(c_{H^+} + a - w)(c_{CH_3COO^-} - w)}{c_{CH_3COOH} + w},$$

where $c_{CH_3COO^-} - w$ is the new concentration in moles per liter of CH_3COO^- ion, after the addition. Naturally, the amount of H^+ ion corresponding to this, and coming from the CH_3COOH, is $c_{H^+} - w$; and the new, larger, amount of un-ionized CH_3COOH is $c_{CH_3COOH} + w$, where c_{CH_3COOH}, c_{H^+} and $c_{CH_3COO^-}$ are the concentrations originally of the un-ionized acid, of H^+ and of CH_3COO^- ions in the pure acid solution.

From this, it will be seen that, if the added acid is large enough in amount, its H^+ ion concentration will drive back the ionization of the CH_3COOH completely, i.e., will make $w = c_{H^+} = c_{CH_3COO^-}$. And so long as the added acid is great enough in concentration, the H^+ ion of the CH_3COOH will not affect its ionization; but if it is of the same order as this, each will mutually affect the ionization of the other. This we shall consider later in another connection.

A similar equation, and similar conclusions, could be obtained for the addition to the acetic acid of a solution of a salt of the acid, in which case at equilibrium there would be an excess of CH_3COO^- ion, and but a small (total) amount of H^+ ion.

It is to be recalled especially, here, that the molecular weight of hydrogen in the allotropic, ionic, state (H^+) is the same as the atomic weight, and is not H_2 as in the gaseous state; and the same is true of practically all elements in the ionic state.

In the above equations, it would seem at first that there is no numerical connection between the various concentrations involved; but that is not true, as can be shown by the following transformations. Let us assume that we start with 1 mole of the acid in v_m liters of solution, and that the percentage of ionization is α. Then $\frac{1-\alpha}{v_m}$ will be the equilibrium concentration of un-ionized acid, and $\frac{\alpha}{v_m}$ will be the equilibrium concentrations of each of the ions formed. We have, then, substituting these values for the c terms above, and simplifying,

$$K_c = \frac{\alpha^2}{(1-\alpha)v_m},$$

which is known as *the Ostwald dilution law.*

In this form, since α can be found from the electrical conductivity, it is possible to test experimentally the truth of the above expressions. Substituting the values of α, so determined, at various dilutions and 25°, Ostwald (Zeit. f. phys. Chem., 3, 170–197, 241–288, and 370–422, 1889) found indeed that K_c for a large number of organic acids is a constant, having a characteristic and different value for each acid; which for acetic acid is equal to 1.8×10^{-5}.

And from this value of K_c, once found in this way, we can then readily find the value of α (percentage of ionization) at any desired dilution of 1 mole in v_m liters, for by evaluating α in the Ostwald dilution law, we find

$$\alpha = \sqrt{K_c v_m + \frac{K_c^2 v_m^2}{4}} - \frac{K_c v_m}{2}.$$

It is also possible here to gain from the Ostwald dilution law an idea of the physical significance of the criterion of equilibrium, K_c, as we did on page 282. Since the numerical value of K_c must, as we found there, be such that when multiplied by 2 it gives the concentration in moles per liter of the acid when it is 50% ionized—we find in this way, that the concentration necessary for a 50% ionization in the case of acetic acid is 2×0.000018 mole per liter; or 1 mole of acid in 27777.5 liters.

While the Ostwald dilution law gives us the variation in the percentage of ionization with the dilution, it is not the only simple form of the law of mass action which correlates the various concentrations, coexisting at equilibrium, nor is it always the most convenient. For example, we usually wish to find the ionic concentrations in the solution, rather than simply the degree of ionization; and to find that by the Ostwald form of the law, it is necessary after finding α from the known v_m, to multiply it (since it is only a percentage), by the concentration, or by the reciprocal of the volume; for $c_H = \alpha \times$ moles per liter of acid $= \alpha \times \frac{1}{v_m}$.

It is clear here that if we start with a certain amount of pure acetic acid in water, and it is ionized to such an extent to give x moles per liter of H^+ ion, we shall also have x moles per liter of CH_3COO^- ion formed, and (original acid $-x$) of un-ionized CH_3COOH left, all coexisting at equilibrium. We can write then

$$K_c=\frac{x^2}{\text{orig. acid}-x};$$

from which, if we know K_c and the original concentration, in moles per liter, of acid, we can solve directly for x and find the number of moles per liter of H^+ ion and of CH_3COO^- ion formed, and the moles of the acid lost by the ionization in a solution of that concentration.

Practically all organic acids give a constant, characteristic, value for the equivalent expressions, $\frac{\alpha^2}{(1-\alpha)v_m}=\frac{x^2}{\text{orig. conc.}-x}$, whether they are mono-, di- or polybasic; at least in the latter cases up to an ionization of 50%. We may conclude, then, that *all polybasic organic acids ionize as monobasic ones (into one mole of* H^+ *ion and* 1 *mole of the negative ion, which still contains replaceable hydrogen) up to that dilution where* α *in this way is* 50%.*

Beyond that point, the further production of H^+ ion, due to a breaking down of the negative ion containing replaceable hydrogen, is great enough in concentration to influence the constant calculated from $K=\frac{\alpha^2}{(1-\alpha)v_m}=\frac{x^2}{\text{orig. conc.}-x}$, which begins to vary. At infinite dilution, naturally, the polybasic acid would be composed of all the replaceable hydrogen as ion, together with the negative radical (without replaceable hydrogen), as the negative ion; in which case, for a tribasic acid we would have $H_3A \rightleftarrows 3H^+ + A^{\equiv}$.

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* In other words, up to that dilution where we have $2K_c$ moles of original acid per liter, i.e., 1 mole in $\frac{1}{2K_c}$ liters of solution; see page 318.

The calculation of the degree of ionization of dibasic acids above the dilution at which $\alpha = 0.5$, has been worked out by W. A. Smith (Zeit. f. phys. Chem., 25, 144, and 193, 1898. See also Wegscheider (Sitz. d. Akad. d. Wissenschaft, 111, 441–510, 1902), McCoy (J. Am. Chem. Soc., 30, 688–694, 1908), and Chandler (*ibid.*, 30, 694–718, 1908)). For a tribasic acid, for example, we have the following processes taking place:

$$H_3A \rightleftarrows H_{,}^{+} + H_2A^{-},$$

$$H_2A^{-} \rightleftarrows H_{,,}^{+} + HA^{=},$$

$$HA^{=} \rightleftarrows H_{,,,}^{+} + A^{\equiv},$$

for which, by application of the law of mass action to each equation, we obtain

$$Kc_{H_3A} = k_1 c_{H_3A} = c_{H,^+} \times c_{H_2A^-},$$

$$k_2 c_{H_2A^-} = c_{H,,^+} \times c_{HA^=},$$

$$k_3 c_{HA^=} = c_{H,,,^+} + c_{A^{\equiv}}.$$

Knowing the values of K (or k_1), k_2 and k_3, we can also find the ionic concentrations produced by the three stages of the process, all of which are dependent upon the total concentration of the system, i.e., all increase with increased dilution. Naturally, the various concentrations can be obtained here either in terms of the percentage of ionization of the original substances and their dilution; or in direct concentrations in moles per liter. The two forms are similar to those above, viz.,

$$K = k_1 = \frac{\alpha_{\prime}^2}{(1-\alpha_{\prime})v_m{}'} = \frac{x^2}{\text{Orig. } c_{H_3A}-x},$$

$$k_2 = \frac{\alpha_{\prime\prime}^2}{(1-\alpha_{\prime\prime})v_m{}''} = \frac{y^2}{x-y},$$

$$k_3 = \frac{\alpha_{\prime\prime\prime}^2}{(1-\alpha_{\prime\prime\prime})v_m{}'''} = \frac{z^2}{y-z}.$$

The use of the α form here is not as convenient as the other, which gives directly the individual concentrations concerned; for although $v_m{}'$ is simply the volume containing 1 mole of the original H_3A, i.e., $\frac{1}{\text{conc. of orig. } H_3A}$, $v_m{}''$, being the volume containing 1 mole of H_2A^-, is equal to the reciprocal of its concentration, viz., $\frac{1}{\alpha_{\prime} \times \text{orig. } H_3A}$; and $v_m{}'''$ is equal to $\frac{1}{\alpha_{\prime\prime} \times \alpha_{\prime} \times \text{orig. } H_3A}$. This unnecessary calculation, in addition to the fact that to get the total concentration of H^+ ion in such a case we would have to make a further calculation, viz.,

$$\text{total } c_{H^+} = c_{H,^+} + c_{H,,^+} + c_{H,,,^+} = \alpha' \times \frac{1}{v_m{}'} + \alpha'' \times \frac{1}{v_m{}''} + \alpha''' \times \frac{1}{v_m{}'''},$$

makes this form of equation less useful than the other.

In the second set of equations, the three successively produced concentrations of H^+, in moles per liter, are simply x, y, and z. Knowing the numerical values of the three constants, and the original concentration of acid, therefore, it is a simple matter to evaluate x, and then, from this and k_2, to find y, and finally, with that and k_3, to find z—and the total concentration of H^+ in the system will be $x+y+z$.

The primary reason for finding the three constants, as above, involving different amounts of H^+ for a tribasic acid, in place of employing a relationship between the total concentration of H^+ present and each of the other constituent ions, is the fact that the constants in this form can be found readily from the acid salts of that acid; for in the case of the salt NaH_2A ionizing into Na^+ and H_2A^- primarily, and then to a lesser degree, by a breaking down of the H_2A^-, into H^+ and $HA^=$, it is possible from determinations of the H^+ content (or of the $HA^=$) to find the constant for the reaction $H_2A^- \rightleftarrows H^+ + HA^=$.

Naturally, here, the further ionization of H_2A^-, for example, into $H_{//}^+$ and $HA^=$, would not be influenced by the $H_/^+$ which is present to the same number of moles per liter as the H_2A^-, from the H_3A, for if it *were* to drive back the ionization reaction $H_2A^- \rightleftarrows H_{//}^+ + HA^=$, it could only form the ionic complex H_2A^-, and that is impossible, since its increased presence, without an equal amount of a positive ion, would make the solution electrically negative—and we know that solutions are always electrically neutral. For this reason the ionization of a definite amount of H_2A^- in a certain volume, into $H_{//}^+$ and $HA^=$, whether produced by the ionization of the acid H_3A, or from the acid salt NaH_2A, would have to be the same. As will be seen, this also justifies our writing the ionization reaction, in such a case as that above, in three steps, and then finding the criterion of equilibrium of each considered by itself.

In general the values of $H_{//}^+$ and $H_{///}^+$ (since the constants k_2 and k_3 are always small compared to $k_1 = K$) are negligible up to such dilutions as will give an ionization of the H_3A into $H_/^+ + H_2A$ a value of 50%, and the same holds true with respect to $H_{//}^+$ for a dibasic acid, and also for the higher values ($H_{////}^+$, etc., for example) for a polybasic acid.

For phosphoric acid we find

$$k_2 = 2 \times 10^{-7} \quad \left(k_2 = \frac{c_{\mathrm{H}''} + c_{\mathrm{HPO}_4=}}{c_{\mathrm{H}_2\mathrm{PO}_4-}} \right),$$

$$k_3 = 1 \times 10^{-12} \quad \left(k_3 = \frac{c_{\mathrm{H}'''} + c_{\mathrm{PO}_4\equiv}}{c_{\mathrm{HPO}_4=}} \right),$$

while for citric acid (tribasic) the following values at 25° were found by Smith:

$$K = 82.0 \times 10^{-5},$$

$$k_2 = \ 3.2 \times 10^{-5},$$

$$k_3 = \ 0.07 \times 10^{-5}.$$

A few ionization constants for organic acids are given below in the table, all referring to the first hydrogen, i.e., are equal to $K_c = k_1$ in the above set of equations.

IONIZATION CONSTANTS OF ORGANIC ACIDS AT 25° C.

	$K \times 10^5$		$K \times 10^5$
Propionic	1.34	Malic	39.5
Isobutyric	1.44	Fumaric	93
Capronic	1.45	Tartaric	97
Butyric	1.49	Salicylic	102
Valerianic	1.61	Orthophthalic	121
Acetic	1.80	Monochloracetic	155
Camphoric	2.25	Malonic	158
Anisic	3.20	Maleic	1170
Phenylacrylic	3.55	Dichloracetic	5140
Succinic	6.65	Oxalic	10060 (±)[1]
Lactic	13.8	Trichloracetic	121000 (±)[1]
Glycollic	15.2		
Formic	21.4		

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[1] These two acids are so largely ionized that a small error in α affects K to a large degree. For a list containing a very large number of other acids, as well as bases, see Landolt-Börnstein-Roth Tabellen, 1912, 1132–1188.

The value of K_c at 18° for a few other acids, some of which are inorganic, but characterized by their small ionization, and by obeying the law of mass action, are given by Walker and Cormack (Trans. Chem. Soc., 77, 8, 1900), the value of acetic acid being given for comparison.

Name.	$K \times 10^{10}$.	Per Cent Ionization in a 0.1 Molar Solution.
Acetic acid (25°), $CH_3COO^-—H^+$	180,000	1.3
Carbonic acid, $H^+—HCO_3^-\,k_1$	3,040	.....
$H^+—CO_3^=\,k_2$	0.6[1]	0.174
Hydrogen sulphide, $H^+—HS^-$	570	0.075
Boric acid, $H^+—H_2BO_3^-$	17	0.013
Hydrocyanic acid, $H^+—CN^-$	13	0.011
Phenol, $H^+—C_2H_5O^-$	1.3	0.0037

[1] McCoy, Am. Chem. Jour., 29, 455, 1903.

The constants (k_2) for the ionization of the second hydrogen ion ($H_{//}^+$) of some acids, H_nA, according to the scheme

$$k_2 c_{H_{n-1}A^-} = H_{//}^+ + H_{n-2}A^=,$$

as found by Chandler are given in the following table:

Acids.	$10^6 k_2$.	Acids.	$10^6 k_2$.
Oxalic	41	*m*-Phthalic	27
Malonic	2.0	Camphoric	14
Succinic	2.2	Itaconic	2.2
Glutaric	3.4	Maleic	0.20
Suberic	3.7	Fumaric	22.0
Pimelic	4.4	Monobromsuccinic	25
Azelaic	3.3	Dibromsuccinic	1540
o-Phthalic	3.1		

These constants were determined by aid of the coefficient of partition between two, immiscible solvents, the $H_{n-1}A^-$, only, being distributed.

The law of mass action, naturally, can also be applied to weak bases, which ionize into the positive radicle and OH^- ion, and for them also a constant value of K_c is found in

$$K_c c_{\text{base}} = c_1 \times c_{OH^-},$$

when c_1 is the concentration of the positive ion (radicle), equal to that of the OH^- ion. And this equation can also be used, just as was the one with acids, to find the displacement in the equilibrium due to the addition of either OH^- ion or of the positive ion, in combination with others. We have then

$$K_c(c_{\text{base}}+w)=(c_1-w+a)(c_{OH^-}-w),$$

where a is the concentration of the positive ion coming from the substance added, and w is the loss in moles per liter in c_1 and c_{OH^-}, and the gain in un-ionized base. The α and x formulas, naturally, can also be applied here as they were for acids.

In the table below are given the values of K_c for a number of bases, as found by experiment.

Urea,	(40°.2)	$K=0.0037\times10^{-11}$
Acetamide,	(40°.2)	0.0033×10^{-11}
Acetanilide,	(40°.2)	0.0044×10^{-11}
Aniline,	(25°)	5.4×10^{-10}
p-Toluidine,	(40°.2)	20.7×10^{-10}
m-Nitraniline,	(40°.2)	4×10^{-12}
p- "	(40°.2)	1×10^{-12}
o- "	(40°.2)	0.01×10^{-12}
Ammonium hydrate, $NH_4^+-OH^-$	(25°)	23×10^{-6}
Methylamine,	(25°)	5×10^{-7}
Dimethalamine,	(25°)	0.074×10^{-5}
Trimethylamine,	(25°)	0.0074×10^{-5}
Propylamine,	(25°)	0.047×10^{-5}
Isopropylamine,	(25°)	0.053×10^{-5}
Isobutylamine,	(25°)	0.034×10^{-5}

Returning now to the consideration of the original expression derived from the law of mass action for a binary electrolyte, viz.,

$$K_c=\frac{c_{\text{ion}}c_{\text{ion}}}{c_{\text{un-ion.}}}=\frac{x^2}{\text{orig. conc.}-x}=\frac{\alpha^2}{(1-\alpha)v_m},$$

where the latter two are especially useful for the calculation of the amount of ionized substance formed when we know K_c and the strength of the substance in solution, while the first is best adapted to finding how the equilibrium is displaced by the addition to the solution of another substance, containing an ion in common.

If we add an acetate (which as we know from Chapter V to be ionized to a very considerable extent) to a solution of acetic acid, where as usual the ionization is small (and can be calculated readily from $K_c = 0.000018$, by either the α or the x form of equation), then, in the equation

$$K_c = \frac{(c_{\mathrm{H}^+} - w)(c_{\mathrm{CH_3COO}^-} - w + a)}{c_{\mathrm{CH_3COOH}} + w},$$

a, the concentration of acet-ion added, will be so large, in comparison with $c_{\mathrm{CH_3COO}^-}$ and with w, that the term, $c_{\mathrm{CH_3COO}^-} - w + a$, will practically be reduced to a, and w will be large enough to be of the same order as c_{H^+} or $c_{\mathrm{CH_3COO}^-}$, i.e., will be great enough to restore the term $c_{\mathrm{CH_3COOH}} + w$ to practically the total value it had before it originally ionized in the water solution of the pure acid. We can write, then, calling the new concentration of hydrogen ion, $c_{\mathrm{H}^+} - w$, $c_{\mathrm{H}}'{}^{+}$

$$K_c = \frac{c_{\mathrm{H}}'{}^{+} \times a}{\text{orig. conc. acid}},$$

or

$$c'_{\mathrm{H}^+} = \frac{K_c(\text{orig. conc. acid})}{a}.$$

In any one concentration of a weak (i.e., slightly ionized) acid, the concentration of H$^+$ *ion is practically inversely proportional to the concentration of the negative ion of its salt which is added to it.* This, naturally, also holds true for a polybasic organic acid, so long as it is ionized to less than 50% and thus behaves as a monobasic acid. Further, it is also true for the $\mathrm{CH_3COO^-}$ ion when a strong (largely ionized) acid is added to the acetic acid—and weak bases can be treated similarly, with a like result as to the concentration of the OH ion or the positive radicle, on the addition of a salt, or of a strong (largely ionized) base.

The effect of an added salt with an ion in common with the acid to which it is added, can be measured experimentally by the change in the H^+ ion concentration by aid of the speed of inversion of sugar, as well as by several methods to be considered later. In this way it is possible to find the actual concentration of the negative ion added to the acid, i.e., to find the value of a in the equations above.

Two acids, when mixed and in the presence of an insufficient amount of base to neutralize both, are found to form H_2O from their H^+ ion contents, with the OH^- of the base, in amounts which are related as their H^+ ion contents are. When such a mixture is evaporated to dryness, and the salts thus formed are separated by use of a suitable solvent, the ratio of the moles of these is also the same as that of the H^+ ion concentrations. In such a case, the final equilibrium attained is the same as that produced by the mixture of one acid with the salt of the other.

When the two acids are organic (or inorganic, so long as they are slightly ionized only) the terms x and x' in the expressions $\frac{x^2}{\text{orig. (1)} - x} = K$, $\frac{x'^2}{\text{orig. (2)} - x'} = K'$, are practically negligible, as compared with the original concentrations of the two acids, hence it is clear that for equal concentrations of two acids when mixed we have

$$\frac{x}{x'} = \frac{\sqrt{K}}{\sqrt{K'}}.$$

The values of x here are, naturally, for the acids in solution alone; when mixed each would affect the other somewhat—this we have not considered. *The neutralizing effect of two acids in a mixture upon an insufficient amount of base to neutralize both, is proportional to the ratio of their* H^+ *ion concentrations, or for weak (slightly ionized) acids to the ratio* $\frac{\sqrt{K_1}}{\sqrt{K_2}}$.

The partition of insufficient acid between two bases, naturally, from the above, will be seen to depend upon the ratio of their OH^- ion content—and for slightly ionized bases, also as above, this will be found to be proportional to the ratio of the square roots of the K values for the bases.

In order that a base may be neutralized to an equal extent by both acids—it is necessary as is self-evident from the above, that they have the same H^+ ion content; in other words $x=\sqrt{Kc_{\text{orig.}}}=x'=\sqrt{K'c'_{\text{orig.}}}$, or, what is the same thing, $Kc_{\text{orig.}}$ must be equal to $K'c'_{\text{orig.}}$ Such solutions are, for example, one of the acetic acid at a dilution of 1 mole in 8 liters, and one of hydrochloric acid at a dilution of 1 mole in 667 liters. These two solutions may be mixed in all proportions without change in the ionic concentrations—and when mixed in equal volumes and treated with a small amount of base, they would produce equal amounts of water; and evaporation to dryness would show that the moles of solid salts formed are the same. Naturally, from what we found in Chapter V, these salts are not formed in the un-ionized state in solution, but remain there partially or wholly ionized, and have nothing to do with causing the reaction to take place; for they may be considered the by-product formed in the production of un-ionized water from the combination of H^+ and OH^-.

That two solutions which are isohydric, i.e., for which $Kc_{\text{orig.}}=K'c'_{\text{orig.}}$, can be mixed in all proportions without change in the ionic concentrations can be seen from the following: Let c and c' be the concentrations of the un-ionized portions of two acids (whose constants are K and K') which are in isohydric solutions, and c_{H^+} and c'_{H^+} be the H^+ ion contents, and c_1 and c_1' be the two negative radicles. Then

$$Kc = c_{H^+} \times c_1,$$

and

$$K'c' = c'_{H^+} \times c_1'.$$

If the volume v of one of these now be mixed with v' of the other, the various final concentrations in the mixture will be:

$$c = \frac{cv}{v+v'};\quad c' = \frac{c'v'}{v+v'};\quad c_1 = \frac{c_1 v}{v+v'};\quad c_1' = \frac{c_1'v'}{v+v'};$$

and

$$c_{H^+} = \frac{c_{H^+} \times v + c'_{H^+} \times v'}{v+v'},$$

and by the substitution of these in the law of mass action above, we find, after simplification,

$$Kc = \frac{c_{H^+} \times v + c'_{H^+} \times v'}{v+v'} c_1 \quad \text{and} \quad K'c' = \frac{c_{H^+} \times v + c'_{H^+} \times v'}{v+v'} c_1'.$$

And since $Kc = K'c'$, by definition, comparison with $Kc = c_{H^+} \times c$, and $Kc' = c'_{H^+} \times c'_1$, shows that c_{H^+} must equal c'_{H^+}, i.e., no displacement of either equilibrium occurs when we mix isohydric solutions of two acids.

An interesting relation has been found by Osaka (Coll. Sci. and Eng. Mem., Kyoto, 1, 103, 1905; 3, 205–210, 1907) to exist between the concentration of H^+ ion (or OH^- ion) in a weak acid (or weak base) when it is 50% neutralized by a strong base (or strong acid). If the acid (or base) is very slightly ionized and the salt practically completely ionized, we have

$$HA+\tfrac{1}{2}Na^{+}+\tfrac{1}{2}OH^{-}=\tfrac{1}{2}H_2O+\tfrac{1}{2}HA+\tfrac{1}{2}Na^{+}+\tfrac{1}{2}A^{-}.$$

Hence in

$$c_{H^+}=\frac{Kc_{HA}}{c_{A^-}}$$

inspection shows that $c_{A^-}=c_{HA}$, and

$$c_{H^+}=K_{\text{acid}}.$$

The concentration of H+ *ion in a weak acid, 50% neutralized by a strong base, is equal to the ionization constant of the acid, provided the salt is practically completely ionized.*

For a weak base, 50% neutralized by a strong acid, we find in the same way

$$c_{OH^-}=K_{\text{base}}.$$

If an equimolecular mixture of two weak acids is 50% neutralized by a strong base and the salts remain practically completely ionized, we shall have

$$HA+HB+Na^{+}+OH^{-}=H_2O+xHA+(1-x)HB \\ +(1-x)A^{-}+xB^{+}+Na^{+}$$

and

$$c_{H^+}=\frac{K_1c_{HA}}{c_{A^-}}=\frac{K_2c_{HB}}{c_{B^-}};$$

but from the chemical equation $c_{HA}=c_{B^-}$, and $c_{HB}=c_{A^-}$.

Hence $$c^2_{H^+}=K_1K_2;\quad c_{H^+}=\sqrt{K_1K_2}.$$

The concentration of H+ *ion in an equimolecular mixture of* *two weak acids, which is 50% neutralized by a strong base, is equal to the square root of the product of the two ionization constants.*

It is also possible, in the same way, to find c_{H+} (or c_{OH-} when the acid (or base) is 1/3, 1/4, or 1/5, etc., neutralized by a strong base (strong acid).

Acids, bases, and salts which are ionized to a considerable extent. Empirical dilution laws.—The application of the law of mass action (the Ostwald dilution law) to the so-called strong (largely ionized) electrolytes does not lead to a constant value for K, when the ionization is taken from the conductivity ratio $\frac{\Lambda_{v_c}}{\Lambda_\infty}$. *As in general the degree of ionization is found to be the same by all of the possible methods, our only conclusion at present is that the law of mass action cannot be applied to the equilibrium of un-ionized and ionized portions in such solutions as these.* Although this is true with regard to very soluble salts, *there is a quantitative relation, which we shall develop below, holding for the ionized portions of difficultly soluble substances.*

Although the Ostwald dilution law fails utterly to hold for the equilibrium between the ionized and un-ionized portions of strong electrolytes, however determined, certain other, *empirical*, dilution laws have been proposed to correlate the amounts of ionized and un-ionized substances coexisting in equilibrium at any dilution. Thus Rudolphi (Zeit. f. phys. Chem., **17**, 385, 1895) found a dilution law which gives a constant value between certain limits, for such solutions as do not follow the Ostwald dilution law. This law written in the α form, as that was, is,

$$\frac{\alpha^2}{(1-\alpha)\sqrt{v_m}} = \text{constant},$$

where the value of the constant is approximately the same for analogous substances. van't Hoff (Zeit. f. phys. Chem., **18**, 300, 1895) altered this to the form

$$\frac{\alpha^3}{(1-\alpha)^2 v_m}=\text{constant},$$

which holds even better than Rudolphi's. Transformed, this relation is

$$\frac{c_i^3}{c_s^2}=\text{constant},$$

i.e., *the cube of the ionic concentration, divided by the square of the un-ionized portion is a constant.*

Writing the Ostwald dilution law in this form we obtain (*for binary electrolytes*)

$$K=\frac{c_i^2}{c_s},$$

while the above empirical relation (in either form) remains the same for binary or ternary substances; in other words, is independent of the number of ions formed from one mole of the substance.

Some of the values calculated by use of van't Hoff's equation are given below. The value of K by the Ostwald dilution law will be found to vary considerably, while the constant of van't Hoff is quite constant, within the experimental error.

$AgNO_3$ 25°

v_m	α	constant of van't Hoff
16	0.8283	1.11
32	0.8748	1.16
64	0.8993	1.06
128	0.9262	1.07
256	0.9467	1.08
512	0.9619	1.09

In 1896 Storch (Zeit. f. phys. Chem., **19**, 13) modified this

Rudolphi form of empirical equation, so as to account somewhat better for the experimental data. He used

$$\frac{(c\alpha)^n}{c(1-\alpha)}=D,$$

where D is a constant, c is the total moles per liter of the electrolyte dissolved, and n, while in general equal to 3/2, varies somewhat with various salts. This form was later modified again by Arrhenius (*ibid.*, 31, 197, 1899) to the form

$$\frac{(c\alpha)^2}{c(1-\alpha)}=D(\Sigma c\alpha)^m,$$

where $m=2-n$ (the n of Storch), and $\Sigma c\alpha$ is the sum of the ion-concentrations due to all electrolytes in the solution. For other forms of general empirical equations, holding for aqueous solutions, see Kendall, Proc. Chem. Soc., **28**, 255, 1912; Trans. Chem. Soc., **101**, 1275, 1912; Med. K. Vet.-Akad. Nobelinstitut, **2**, 38, 1913; and Jour. Am. Chem. Soc., **36**, 1069, 1914.

In addition to these more or less general equations, at least as far as concerns aqueous solutions, two forms of equation have been proposed which hold, the one particularly well for KCl, and the other very satisfactorily for both KCl and NaCl, *at all temperatures*. Thus Bancroft (Zeit. f. phys. Chem., **31**, 188, 1899) proposes a dilution law of the form

$$\text{constant}=\frac{C_i^n}{C_s},$$

in which the constant and n are functions of the nature of the electrolyte, which holds in a remarkable way for KCl at 18°

when in the form $\frac{c_i^{1.36}}{c_s} = 2.63$, as is shown by the following table:

KCl SOLUTIONS AT 18°

$$\frac{c_i^{1.36}}{c_s} = 2.63.$$

α.		v_m
Obs.	Calc.	
0.987	0.987	10000
0.984	0.983	5000
0.978	0.976	2000
0.973	0.970	1000
0.965	0.962	500
0.950	0.948	200
0.934	0.934	100
0.915	0.917	50
0.902	0.906	33.3
0.883	0.892	20
0.853	0.864	10
0.821	0.834	5
0.803	0.813	3.3
0.780	0.786	2
0.748	0.745	1
0.706	0.700	0.5
0.673	0.672	0.3

For other substances the relation $\frac{c_i^n}{c_s}$, however, is not so satisfactory or constant.

Noyes (Jour. Am. Chem. Soc., **26**, 168, 1904) finds that for the chlorides of sodium and potassium at various temperatures give a constant value for the ratio $\frac{1-\alpha}{c^{\frac{1}{3}}}\left(\text{where } \alpha = \frac{\Lambda_{v_e}}{\Lambda_\infty}\right)$; that is, *the fraction of salt un-ionized is directly proportional to the cube root of the concentration; or the concentration of un-ionized substance, $c(1-\alpha)$, is directly proportional to the 4/3 power of the total concentration of salt, c.* The degrees of ionization of KCl and NaCl were found experimentally here to be nearly identical (the extreme variation being 2%) *at all temperatures and dilutions.* In a 0.1 molar the ionization has approximately the following values:

18°	84%	281°	67%
140°	79%	306°	60%
218°	74%		

The values of constant $= \frac{1-\alpha}{c^{\frac{1}{3}}}$ are

	18°	140°	218°	281°	306°
NaCl..........	0.366	0.448	0.573	0.745	0.877
KCl............	0.321	0.468	0.577	0.713	0.853

In view of these and other facts Noyes (Carnegie Publication, No. 63, 1907) concludes that in solutions of such strong (largely ionized) electrolytes the form of union represented by the un-ionized portion of a substance differs essentially from ordinary chemical combinations, it being so much less intimate, that the ions still exhibit their characteristic properties, at least so far as these are not dependent upon their existence as separate aggregates. In other words, the law of mass action is inapplicable to the relation between ionized and un-ionized portions as they exist in strong electrolytes, and hence this is not to be considered as a purely *chemical* equilibrium, for which, as we have seen, the law of mass action appears to hold rigidly.

The culmination of all empirical forms of dilution law, *in that it holds not only for aqueous, but also for non-aqueous solutions of strong electrolytes*, is that which has been recently applied by Kraus and Bray (Jour. Am. Chem. Soc., **35**, 1315–1434, 1913), and which was first proposed by Kraus in 1908, and also found later and independently by MacDougal (*ibid.*, **34**, 855, 1912). This form, in our notation is

$$\frac{(c\alpha)^2}{c(1-\alpha)} = K + D(c\alpha)^m,$$

where c is the concentration of salt, α the degree of ionization from $\frac{\Lambda_{v_c}}{\Lambda_\infty}$, and K, D, and m are characteristic constants.

In sufficiently dilute solutions, the term $(c\alpha)^m$ becomes negligible here in comparison with K, and the equation approaches the Ostwald dilution law as a limit; while in concentrated solutions, K becomes negligible, as compared with $D(c\alpha)^m$, and the equation approaches the empirical form of Storch-Arrhenius. The constants of the equation for any one case here can be readily evaluated from the experimental data for Λ_{v_c}, Λ_∞ and c, by a graphical method.

The striking thing about this form of equation is that it enables us to understand the minimum of equivalent conductivity often observed in non-aqueous solvents—indeed if m is greater than unity, the equivalent conductivity must pass through a minimum value; while when m is less than unity, the equivalent conductivity must decrease continually with increasing concentration.

Although no higher valence types of salt have been studied in connection with this equation, owing to the lack of experimental data, and the probability of the formation of intermediate ions; there is reason to believe that they also will obey the same law as do binary electrolytes.

Heat of ionization.—By the van't Hoff equation, it is possible to calculate the heat of ionization of a substance, *provided we know the degrees of ionization of any one identical concentration at two temperatures.* This is true not only for those substances which follow the Ostwald dilution law, but also for all others as well, according to Arrhenius (Zeit. f. phys. Chem., **4**, 96, 1899, and **9**, 339, 1892). For binary electrolytes then, we have (page 261)

$$Q_v = \frac{R \times 2.303(\log K' - \log K)T'T}{T - T'},$$

where $K' = \frac{\alpha'^2}{(1-\alpha')v_m}$ and $K = \frac{\alpha^2}{(1-\alpha)v_m}$ (the terms v_m being identical in both equations) represent the change in ionization with the temperature *for this dilution*, even though they would not represent the facts if considered at other dilutions. It is for this reason, that it is immaterial here, what law the concentrations of ions and un-ionized substance follow with varying dilution; all substance under these conditions can be treated similarly.

Q_v in this equation, then, is the heat evolved when a mole of substance ionizes in solution, at a temperature equal to the mean of those at which the K_c' and K_c values are calculated. It will be observed here that these values differ from those calculated from the table given on page 245, for these refer to the heat of formation of the ions from substance already in solution, while those referred to the more complex process of solution *and* ionization, i.e. referred to the difference in energy between the ionized state, and the solid or gaseous state. Some of the values as calculated in this way by Arrhenius are given below, the unit being the small calorie:

HEATS OF IONIZATION

Substance.	Temperature.	Calories (calc.).
Acetic acid	35°	386
	21°.5	−28
Propionic acid	35°	557
	21°.5	183
Butyric acid	35°	935
	21°.5	427
Phosphoric acid	35°	2458
	21°.5	2103
Hydrofluoric acid	33°	3549
Potassium chloride	35°	362
" iodide	35°	916
" bromide	35°	425
Sodium chloride	35°	454
" hydrate	35°	1292
" acetate	35°	391
Hydrochloric acid	35°	1080

The ionization of a substance in solution thus usually takes place with an evolution of heat.

HEAT EVOLVED BY THE COMPLETION OF THE IONIZATION (1 MOLE IN 200 MOLES OF WATER)

Substance.	Temperature.	Calories (calc.).
Potassium bromide	35°	58
" iodide	35°	132
" chloride	35°	56
Sodium hydrate	35°	180
" chloride	35°	81
Hydrochloric acid	35°	136
Hydrofluoric acid	33°	3304
Phosphoric acid	21°.5	1682

Above (p. 243) it was noted that the heat of neutralization of an acid by a base is made up of the heat of association of H^+ and OH^- ions ($137K$) plus the heat of association of the salt formed, plus the sum of the heats evolved in the completion of the ionizations of the acid and base. We are now in the position to test this relation quantitatively, for we can now calculate the heats of ionization of the acid, base, and salt. This relation can be expressed mathematically in the following simple form:

$$Q_{\text{neut.}} = 13700 - w_3(1-\alpha_3) + w_2(1-\alpha_2) + w_1(1-\alpha_1) \text{ cals.},$$

where the figures 1, 2, and 3 refer respectively to acid, base, and salt, and $w_3(1-\alpha_3)$, the heat evolved by the *ionization* of the salt, is subtracted because its *negative* value is equal to the heat of *association* from the ions of the salt required in the relation. The table given below is self-explanatory, and certainly shows conclusively that, as was mentioned before, *the value of the heat of neutralization of an acid by a base cannot be considered as indicative of the strength of the acid.* The two latter are relatively weak acids and yet they give rise to the greatest amount of heat.

HEAT OF NEUTRALIZATION OF ACIDS WITH NaOH

(1 equivalent of acid+1 equivalent of NaOH+400 moles of H_2O)

	At 35°. Calc.	At 21.5°.	
		Calc.	Obs.
HCl	12867	13447	13740
HBr	12945	13525	13750
HNO_3	12970	13550	13680
CH_3COOH	13094	13263	13400
C_2H_5COOH	13390	13598	13480
$CHCl_2COOH$	14491	14930	14830
H_3PO_4	14720	14959	14830
HF [1]	16184	16320	16270

[1] For data as to the ionization of HF, see Deussen, Zeit. f. anorg. Chem., 44, 408, 1905.

We have found thus that the van't Hoff equation can be used for the calculation of the heats of *dissociation* or *ionization;* it can also be used for heats of *solution*, when the substance is either completely ionized or completely un-ionized. So far, however, it has been found impossible to calculate the heats of *solution* of substances which are *partly* ionized.

Solubility or ionic product.—Although, as we have seen, the law of mass action cannot in general be applied to the equilibrium of the ionized and un-ionized portions of a substance in solution (except to organic, or slightly ionized inorganic, acids and bases), it *can* be applied with considerable accuracy to a very large number of saturated solutions. An example of such an equilibrium is a saturated solution of silver chloride, which is found to be practically completely ionized according to the scheme

$$AgCl \rightleftarrows Ag^+ + Cl^-.$$

Applying the law of mass action to this we obtain

$$Kc_{AgCl} = c_{Ag^+} \times c_{Cl^-},$$

when c_{AgCl} is the concentration of un-ionized AgCl, c_{Ag^+} that of the Ag^+ ion, and c_{Cl^-} that of the Cl^- ion. Since the solution is saturated, the value of c_{AgCl} at any temperature must remain constant, for if the solution were unsaturated, solid would dissolve; if supersaturated, solid would precipitate. We have then, at any one temperature, in a saturated solution of silver chloride, the relation

$$Kc_{AgCl} = \text{constant} = c_{Ag^+} \times c_{Cl^-};$$

i.e., *in a saturated solution of a binary electrolyte* (*of this kind*) *the product of the concentrations of the ions must remain constant, with unchanged temperature.* This product is equal, here, to the square of the solubility of the AgCl, since this is completely ionized in such a high dilution, into 1 mole of Ag^+ ion and 1 mole of Cl^- ion, for each mole of AgCl originally present.

Expressing this in a more general form, we have for the reaction

$$A_{N_1}B_{N_2} \rightleftarrows N_1A + N_2B$$

in a saturated solution,

(26) $$c_A^{N_1} c_B^{N_2} = \text{constant} = s,$$

where s, if the $A_{N_1}\,B_{N_2}$ is completely ionized, would be equal to $(N_1 \text{ times the solubility of } A_{N_1}B_{N_2})^{N_1} \times (N_2 \text{ times the solubility of } A_{N_1}B_{N_2})^{N_2}$, since these terms represent the concentrations of A and B, each raised to its proper power.

This term s was called by Ostwald *the solubility-product of the substance.* The solubility-product, of a substance which may be defined as *the greatest possible product of the concentrations of the constituent ions according to* (26) *which can exist at any one temperature*, is of paramount importance in analytical chemistry, *for a precipitate* (*when due to an ionic reaction, and most of them can be shown to be due to that*) *is always and only formed when its solubility-product is exceeded.* This, of course, presupposes that no supersaturation phenomenon is possible; if it is, then the *metastable limit* (p. 160) must first be exceeded.

Stieglitz (Jour. Am. Chem. Soc., **30**, 946–954, 1908) points out in this connection that even if the un-ionized portion does not remain constant, as we have assumed it to above, it is an empirical fact that the *product of the concentrations of the ions* (26), *the solubility-product, is a constant*, and the solubility-product law may be considered as empirical. Washburn, on the other hand (*ibid.*, **32**, 487–8, 1910), shows that the solubility-product law can be derived theoretically, without the assumption that the law of mass action holds, and also without any idea as to what law does regulate the equilibrium between *un-ionized substance* and *the ionized products.* The fault of the complete form of the law of mass action, as applied to these slightly soluble but highly ionized substances, lies, then, in the concentration of the un-ionized substance, rather than in the concentrations of the ionized products which coexist at equilibrium.

It seems to be difficult for one who first encounters this concept of solubility-product, to see why it should mean any more, or be any more valuable, than the solubility itself, to which it is so simply related when the ionization of the salt in pure water is complete. Perhaps the best way to realize the difference in the two quantities here, is to recall the fact that while the *solubility* itself is changed by the presence of a substance containing an ion in common with it, and consequently has no fixed, constant, value except when the salt is dissolved in pure water, i.e., when we have, for the AgCl case, an equal concentration of Ag^+ and Cl^- ions; *the solubility-product remains constant, not only when the ionic concentrations are identical, but also when one of them is present in any desired excess*, as would be the case when another substance, with an ion in common with the salt, is added to its solution. We see from this, then, that while *for this case* the solubility has no *general* meaning, the *square of the solubility* is always equal to the product of the final ionic concentrations; and this remains unaltered, no matter what their original amounts might have been, due to the addition of either from another source. Naturally, all this would also be true in a more complicated case, i.e., where the relationship between solubility and solubility-product is not so simple.

Just as we found a decrease in the dissociation of a gas or an organic acid by the addition of one of the products of the reaction from an exterior source, so here the addition of a substance with an ion in common causes the formation and *separation* in the solid state of the un-ionized substance. For the term s must still retain its constant value, and consequently the constituent ions of the substance must unite to form more of the un-ionized portion, which, since the solution is already saturated with it, separates out as solid. This has been found to be true by experiment, *but only true for those substances which are difficultly soluble.* The effect may be observed most easily by dissolving the difficultly soluble substance in a solution of the salt with an ion in common; but it can also be attained by adding to the saturated water solution of the substance a strong solution of the salt, when a precipitation of the already dissolved substance, usually in the crystalline state, will be observed. Thus if we add to one portion of a saturated solution of silver acetate a strong solution of sodium acetate containing x moles of CH_3COO^- ion, and the same amount of a solution of silver nitrate containing x moles of Ag^+ to the liter to another equal portion, we observe an equal precipitation of solid silver acetate in the two solutions.

Although all this is true, as far as the precipitation is concerned for all saturated solutions, it is only for the difficultly soluble substances that these quantitative relations are found to hold.

The examples below will serve to show how the solubility product of a substance can be found, and how when once found can be employed to foresee the solubility of the substance in a solution already containing a common ion.

Silver bromate is soluble at 25° to the extent of 0.0081 mole per liter. Assuming the ionization in this state to be practically complete, and it certainly is nearly so, since all uni-univalent salts are at that dilution, the concentration of the ions Ag^+ and BrO_3^- will be the same, and equal each to 0.0081 mole per liter. The solubility product at this temperature, then, will be

$$(0.0081)(0.0081) = s_{AgBrO_3}.$$

The solubility of $AgBrO_3$ in a solution of silver nitrate containing 0.1 mole of Ag^+ ion (or in potassium bromate containing 0.1 mole of BrO_3^- ion) can be found, then, by aid of the relation

$$(0.0081)^2 = (0.0081 + 0.1 - w)(0.0081 - w),$$

and is equal to $(0.0081 - w)$, for that is the concentration of Ag^+ and BrO_3^- ions now existing in the solution, and coming from the salt; the amount 0.1 of one being due to the other salt, and w being the $AgBrO_3$, which would otherwise have dissolved in the water, but which now remains undissolved owing to the presence of this 0.1 mole of Ag^+ or BrO_3^-.

Where the substance dissociates into more than two ions and can be assumed to be completely ionized, the relation is quite similar. Suppose the salt to dissociate according to the scheme

$$MA_3 \rightleftarrows M^{+++} + 3A^{-},$$

and not to form any intermediate ion. As solubility product we shall have, if sol. is the solubility of the completely ionized salt MA_3 in pure water,

$$(\text{sol.}) \times (3\ \text{sol.})^3 = s_{MA_3},$$

or

$$c_{M^{+++}} \times c_{A^-}^{3} = s_{MA_3},^*$$

for we must have three times the number of moles per liter of A^- that we have of M^{+++}, according to the chemical equation, i.e.,

$$c_{M^{+++}} = \text{sol.} \quad \text{and} \quad c_{A^-} = 3\ \text{sol.}$$

In case 0.1 mole of one of the ions is present from another source, we would have, then,

$$(c_{M^{+++}} + 0.1 - w)(c_{A^-} - 3w)^3 = s_{MA_3}$$

or

$$(c_{M^{+++}} - w')(c_{A^-} + 0.1 - 3w')^3 = s_{MA_3},$$

from which it is apparent that the effect of equal addition is not the same for the two ions, i.e., that w and w', the decreases in the solubility of the MA_3 in the two cases, are not equal.

In case the substance is not completely ionized, the solubility product is not so directly related to the solubility of the substance as in the above cases, i.e., to the square in one

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[*] S_{MA_3} here, is equal then to $27(\text{sol.})^4$, where sol. is the solubility in moles per liter of pure water of the salt MA_3, which after solution ionizes practically completely.

case and twenty-seven times the fourth power in the other. Consider the case of uric acid, which, at 25°, is soluble to 0.0001506 mole per liter, and is ionized in that condition to 9.5% into H^+ and the negative radicle, which we shall designate as U^-. The solubility product here is naturally

$$(0.0001506 \times 0.095)(0.0001506 \times 0.095) = s_{HU} = K_{HU}(0.0001506 \times 0.905),$$

where we use the s_{HU}, the product of the two constants at this temperature, i.e., K_{HU} multiplied by 0.0001506×0.905, the un-ionized portion.

The solubility of uric acid in a molar solution of hydrochloric acid, for which $\alpha = 0.78$ (i.e., $H^+ = 0.78$, $Cl^- = 0.78$), is to be found in the following way:

$$(0.0001506 \times 0.095 + 0.78 - w)(0.0001506 \times 0.095 - w) = (0.0001506 \times 0.095)^2 = s_{HU},$$

where $(0.0001506 \times 0.095 - w)$ represents the present concentration of H^+ and U^- from the uric acid, while its total solubility in the hydrochloric acid solution is

$$(0.0001506 \times 0.905) + (0.0001506 \times 0.095 - w),$$

i.e., *the total solubility is equal to the sum of that which is un-ionized, and that which is ionized.*

Just as for organic acids in general, an infinite excess of one of the ions will cause the ionization of the substance to become zero. *It is to be observed here, however, that this excess will only cause the solubility to become zero in the case that the ionization is complete.* In the case of uric acid, an infinite amount of H^+ or U^- at best can reduce the solubility by only 9.5%, the remaining 90.5% being un-ionized and not affected at that temperature by any addition of substance which does not react chemically with it.

That a substance is *always* decreased in solubility by the addition to it of a substance with an ion in common is not true, as the well-known behavior of silver cyanide in potassium cyanide will show. In all such cases, however, the equilibrium which has previously existed is altered in some way, so that the relations are not the same. These cases are usually characterized by the formation of a complex ion, the *existence product* of which is exceeded. The removal of the ions to form this complex ion disturbs the equilibrium of the difficultly soluble salt; the un-ionized portion, then, ionizes further, and its loss is replaced by the solid phase. This process continues, dissolving new salt, until equilibrium is attained, i.e., until the existence product, if the substanc be un-ionized in place of difficultly soluble, whatever it may be, is just satisfied; when solution ceases. The ionization of silver potassium cyanide takes place almost completely according to the scheme

$$KAgCN_2 = K^+ + AgCN_2^-,$$

but it has been found that in a 0.05 molar solution we have Ag^+ ion to the extent of 3.5×10^{-11} and CN^- to 2.76×10^{-3} moles per liter.

Knowing the concentration of the metal ion, for example (which can be determined by methods given in the next chapter), in the complex salt solution and in a water solution of the difficultly soluble salt, we can foresee the behavior of that salt when in a solution of a salt which might dissolve it to form a complex solution of that strength. In general, i.e., *when the concentration of the metal ion in a water solution of salt is greater than that of a water solution of a complex salt, the simple salt will dissolve in any solution which will produce the complex salt in this concentration. If the concentration of the metal ion is* *smaller, the solid will not dissolve to any greater extent than it does in pure water, for the ionic product of the complex ion cannot be exceeded.*

By this law it is possible to find the relative solubility of salts of the same metal in water. Thus silver sulphide is the only silver salt which will not dissolve in potassium cyanide solutions; in other words, is the most insoluble salt of silver, and contains less Ag^+ ion in its saturated solution than exists even in a solution of silver potassium cyanide such as that given above.

It is not only for substances in solution that we find this constancy of the product of the concentrations of the ions, for it also exists in our usual solvent, water, where the ionized portion is so small that the un-ionized portion may be considered as constant, i.e., $1-\alpha=1$. Expressing the concentrations of H^+ and OH^- ions in a liter of water by c_1 and c_2, and the un-ionized portion, which is practically 1 liter, by $\frac{1000}{18}=55.5$ moles, we have

$$c_1c_2=K_{H_2O}55.5=s_{H_2O}=\text{constant}.$$

The value of $c_1=c_2=H^+$ $(=OH^-)$ ion in water at various temperatures, as given by Noyes (Carnegie Publication, No. 63, 1907), is as follows:

Temp.	$c_1\times 10^7$. Moles per Liter.	Temp.	$c_1\times 10^7$. Moles per Liter.
0°	0.30	100°	6.9
18°	0.68	156°	14.9
25°	0.91	218°	21.5
		306°	13.0

Here the maximum value of s_{H_2O} appears to lie between 250° and 275°, above which point it decreases.

The *ionic* or *existence products* (we can hardly call them solubility products), then, are as follows:

$$s^{\circ}=(0.30\times10^{-7})^2, \qquad s_{156}{}^{\circ}=(14.9\times10^{-7})^2,$$
$$s_{18}{}^{\circ}=(0.68\times10^{-7})^2, \qquad s_{218}{}^{\circ}=(21.5\times10^{-7})^2,$$
$$s_{25}{}^{\circ}=(0.91\times10^{-7})^2, \qquad s_{306}{}^{\circ}=(13\times10^{-7})^2.^{*}$$
$$s_{100}{}^{\circ}=(6.9\times10^{-7})^2,$$

Knowing the solubility products of two substances with an ion in common, it is possible to find how much of each will dissolve when they are exposed together to the action of a solvent; and this, of course, may be expanded to three or more substances together. Here, since the concentrations are of the same order, each salt will affect the solubility of the other, i.e., we cannot tell directly just what amount of either salt will finally be present to affect the other.

The general method of treatment necessary in such a case is to assume a certain amount of each salt as present in the final equilibrium, and then to state the criteria of equilibrium in these terms and solve for them in the two equations. Assume we have the two completely ionized, difficultly soluble salts MA and MA_1, with the ion M^+ in common, and that they are dissolved simultaneously in water. Call the amount of MA which dissolves x, and the amount of MA_1 y. In the solution then we must have $x+y$ moles per liter of M^+ ion, x of A^- and y of $A_1{}^-$; and, if s_{MA} and s_{MA_1} are the respective solubility products, the relations must be

$$x(x+y)=s_{MA},$$

$$y(x+y)=s_{MA_1},$$

so that by solving the simultaneous equations we can find x and y. Naturally, if the ionization is not complete, we may still represent the ionized portions by x and y, and then after finding the degree of ionization when mixed, if that is possible, we can calculate the total amount of each dissolved.

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* See also Heydweiller, Ann. Phys. (IV) 28, 503-512, 1909.

An example of the above calculation is given by the simultaneous solution of thallium chloride and thallium sulphocyanate. The solubilities in water, each for itself, are $TlCl = 0.0161$ and $TlSCN = 0.0149$, both in moles per liter. Assuming complete ionization, the solubility products are then respectively $(0.0161)^2$ and $(0.0149)^2$, and if x represents the amount of chloride and y that of sulphocyanate dissolving from the mixture, we have $x+y=Tl^+$, $x=Cl^-$, and $y=SCN^-$, and

$$x(x+y)=(0.0161)^2,$$

$$y(x+y)=(0.0149)^2,$$

from which we find $x=0.0118$ and $y=0.0101$, while the values $x=0.0119$ and $y=0.0107$ are found by experiment.

In case we had the two salts

$$MA = M^+ + A^- \text{ and } BA_2 = B^{++} + 2A^-,$$

both of which are practically completely ionized, and we assume z moles of the first and w moles of the second to coexist in the equilibrium state when dissolved simultaneously, we would have $c_{M^+}=z$, $c_{B^{++}}=w$, $c_{A^-}=z+2w$, and can write

$$z(z+2w)=s_{MA},$$

$$w(z+2w)^2=s^2_{BA_2},$$

from which, knowing the numerical values of the terms s from the solubilities alone in pure water, we could solve for z and w.

There is difficulty observed in many cases here, and this is possible in the application of the law of mass action in general, due to the formation of intermediate ions, and in such cases, of course, the above law does not hold, unless these are also taken into account. Thus PbI_2 follows the law rigidly, ionizing as it does almost completely into Pb^{++} and $2I^-$; but $PbCl_2$, on the other hand, fails to follow the law, owing apparently to the existence of the intermediate ion $PbCl^-$, for the ionization scheme is not the same as for PbI_2, although both are of the same type as BA_2.

With respect to the addition of a salt to such a system, when the salt added does not contain an ion in common, there is little known that is general. In such cases an increased solubility at times may be observed, owing to the entire rearrangement of the equilibrium, such as that due to a chemical reaction taking place between the dissolved salts.

For actual applications and the limitations of this law, see Noyes, Bray and others (Jour. Am. Chem. Soc., 33, 1639–1686, 1911), Harkins and Winninghoff (*ibid.*, 33, 1807–1873). Sherrill, *ibid.*, 32, 741–748, 1910), and Kendall (Proc. Roy. Soc. A., 85, 200, 1911). And for a list of the numerical values of the solubility product, see Landolt-Börnstein-Roth, Tabellen, 1912, pages 1199–1204.

Hydrolytic dissociation. Hydrolysis. — Hydrolysis is the process taking place in the water solution of a *salt*, which causes the solution to appear alkaline or acid, or results in a neutral equilibrium according, for example, to the scheme

$$MA + H_2O \rightleftarrows MOH + HA,$$

where both the acid and base formed are but slightly ionized.

If the acid formed is difficultly soluble, or but slightly ionized, the base being ionized, the reaction will be alkaline (OH^- ion). When the base is difficultly soluble or but slightly ionized, and the acid ionized, the reaction is acid (H^+ ion). And, finally, if both acid and base are difficultly soluble or but slightly ionized, practically equal amounts of H^+ and OH^- as ion will be removed from the solution, and consequently the reaction will be practically neutral. In other words, then, hydrolysis is the result of the removal of either H^+ or OH^- ion (or both) from the water by the A^- or M^+ ion of the salt, to form un-ionized or insoluble acid, base (or both).

Examples of this process are most common. For instance, the solutions of all mercury, copper, zinc, etc., salts are acid, for an un-ionized basic substance is formed by the reaction, leaving free, ionized acid; and a potassium cyanide solution is alkaline, owing to the formation of un-ionized hydrocyanic acid and ionized potassium hydrate. The most striking example of this process, perhaps, is the precipitation of bismuth oxychloride when water is added to a hydrochloric acid solution of the chloride, but the basic acetate separation of iron is just as characteristic, although at first sight not so direct.

Since we know the conditions under which, in general, insoluble or un-ionized substances will form, i.e., by the exceeding of their solubility products or analogous values, it is possible to find the conditions necessary to produce a hydrolytic dissociation. And since we know also when these substances will cease to form, we can also find the equilibrium which must be attained as the result of that hydrolytic dissociation.

We recognize at once that if the product of the concentrations of M^+ and OH^- ions is larger than that which can exist in a pure water solution of MOH, un-ionized substance must form. By this formation, however, the equilibrium of H^+ and OH^- ions will be disturbed, and a further ionization of water must take place, until at length the ionic product is again just attained. If the H^+ and A^- ions at this point do not unite to form un-ionized acid, the further ionization of water will be unlike what it would be in the absence of this excess of H^+ ion, for, since $c_{H^+} \times c_{OH^-}$ must at the same time be equal to s_{HO_2}, we can only have $\frac{s_{H_2O}}{c_{H^+}}$ moles per liter of OH^- ion present, when c_{H^+} is the total concentration of H^+ ion at that time.

The reaction caused by the formation of un-ionized or insoluble acid, when no un-ionized base is formed, or forms but slightly, is exactly analogous to the above. In both cases water is decomposed, owing to the removal of one of its ions, and the further ionization of water and formation of the insoluble or un-ionized base or acid continues until the equations of equilibrium are fulfilled.

For the sake of simplicity we shall consider separately the cases that the reaction is caused primarily by the base, primarily by the acid, or by both base and acid.

Case I. *The formation of un-ionized or insoluble base is the direct cause of the hydrolytic dissociation, and the acid formed is largely ionized.* By definition, here, hydrolysis, which may occur according to one of the three typical equations,*

$$(a) \qquad MA+H_2O \rightleftarrows MOH+HA,$$

$$(b) \qquad MA_2+2H_2O \rightleftarrows M(OH)_2+2HA,$$

$$(c) \qquad MA_3+3H_2O \rightleftarrows M(OH)_3+3HA,$$

must occur when the product—depending upon the valence of the positive ion of the salt—

$$c_{M^+} \times c_{OH^-},$$

$$c_{M^{++}} \times c^2_{OH^-},$$

or

$$c_{M^{+++}} \times c^3_{OH^-},$$

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* The reader can calculate for himself, after studying the following pages, the changes that would be caused if the negative radical A were di- or trivalent. See also Hill, Trans. Chem. Soc., 89, 1273–1289, 1906.

is greater than that which can exist in the absence of un-ionized base, for then un-ionized base must form. And the formation of base (and acid) must continue until equilibrium is established *in the solution*, i.e., until the condition, for (*a*), (*b*), or (*c*),

$$\text{final } c_{\mathrm{M}^+} \times \text{final } c_{\mathrm{OH}^-} = K_{\mathrm{MOH}} \times c_{\mathrm{MOH}} \text{ formed},$$

$$\text{final } c_{\mathrm{M}^{++}} \times (\text{final } c_{\mathrm{OH}^-})^2 = K_{\mathrm{M(OH)_2}} \times c_{\mathrm{M(OH)_2}} \text{ formed},$$

or

$$\text{final } c_{\mathrm{M}^{+++}} \times (\text{final } c_{\mathrm{OH}^-})^3 = K_{\mathrm{M(OH)_3}} \times c_{\mathrm{M(OH)_3}} \text{ formed},$$

is fulfilled.

In case the base formed is difficultly soluble, since the criterion of equilibrium holds for the substance in solution, i.e., for a homogeneous equilibrium, the above conditions would naturally simplify to the following:

$$\text{final } c_{\mathrm{M}^+} \times \text{final } c_{\mathrm{OH}^-} = s_{\mathrm{MOH}},$$

$$\text{final } c_{\mathrm{M}^{++}} \times (\text{final } c_{\mathrm{OH}^-})^2 = s_{\mathrm{M(OH)_2}},$$

or

$$\text{final } c_{\mathrm{M}^{+++}} \times (\text{final } c_{\mathrm{OH}^-})^3 = s_{\mathrm{M(OH)_3}},$$

the excess of un-ionized base formed separating out as a solid, leaving its concentration *in solution* constant.

In addition to the above equilibria in the solution, we must also always have the condition

$$c_{\mathrm{H}^+} \times c_{\mathrm{OH}^-} = s_{\mathrm{H_2O}}$$

fulfilled, where the concentration of the H^+ ion is primarily fixed by the hydrolytic dissociation, the smaller amount of free OH^- depending upon that and the value of $s_{\mathrm{H_2O}}$ at that temperature. Hence it is evident that the final concentration of OH^- ion, from the slightly ionized base, as well as from water, can always be readily found by dividing $s_{\mathrm{H_2O}}$, at the temperature in question, by the final concentration of H^+ ion, which is dependent only upon the extent of the hydrolysis, i.e., upon the extent to which the salt is decomposed by the reaction with water, and the ionization of the acid at the concentration to which it is formed.

If we designate by α the percentage of salt hydrolyzed, i.e., the percentage of the salt decomposed by water according to one of the above chemical reactions, by d_s the ionization of the salt left, and by d_A the ionization of the acid, i.e., the fraction of the acid formed which remains ionized, the final concentration of M^+, M^{++}, or M^{+++} ion, from an original concentration of salt of 1 mole in v_m liters, will be $\frac{d_s(1-\alpha)}{v_m}$, and that of the un-ionized base, which causes the reaction, will be $\frac{\alpha}{v_m}$. The total acid formed will be $\frac{\alpha}{v_m}$ for (*a*), $\frac{2\alpha}{v_m}$ for (*b*), and $\frac{3\alpha}{v_m}$ for (*c*), the concentration of H^+ ion being respectively $\frac{d_A\alpha}{v_m}$, $\frac{2d_A\alpha}{v_m}$, and $\frac{3d_A\alpha}{v_m}$.

We have, then, substituting these values in the above conditions of equilibrium $\left(\text{remembering that } c_{OH^-} = \frac{s_{H_2O}}{c_{H^+}}\right)$, when the base is not difficultly soluble,

$$\frac{d_s(1-\alpha)}{v_m}\,\frac{s_{H_2O}}{d_A\frac{\alpha}{v_m}} = K_{MOH}\frac{\alpha}{v_m},$$

$$\frac{d_s(1-\alpha)}{v_m}\left(\frac{s_{H_2O}}{2d_A\frac{\alpha}{v_m}}\right)^2 = K_{M(OH)_2}\frac{\alpha}{v_m},$$

$$\frac{d_s(1-\alpha)}{v_m}\left(\frac{s_{H_2O}}{3d_A\frac{\alpha}{v_m}}\right)^3 = K_{M(OH)_3}\frac{\alpha}{v_m};$$

and when the base is difficultly soluble, i.e., when the solubility product may be substituted for the product of ionization constant and concentration of un-ionized base,

$$\frac{d_s(1-\alpha)}{v_m}\,\frac{s_{H_2O}}{d_A\dfrac{\alpha}{v_m}} = s_{MOH},$$

$$\frac{d_s(1-\alpha)}{v_m}\left(\frac{s_{H_2O}}{2d_A\dfrac{\alpha}{v_m}}\right)^2 = s_{M(OH)_2},$$

$$\frac{d_s(1-\alpha)}{v_m}\left(\frac{s_{H_2O}}{3d_A\dfrac{\alpha}{v_m}}\right)^3 = s_{M(OH)_3}.$$

By simplification of these six conditions, grouping the constant terms together, we find

$$\left.\begin{aligned}
&\frac{\alpha^2}{(1-\alpha)v_m}\cdot\frac{d_A}{d_s}=\frac{s_{H_2O}}{K_{MOH}}=\text{constant} \quad \text{when the base MOH is soluble}\\
&\text{or}\\
&\frac{\alpha}{(1-\alpha)}\cdot\frac{d_A}{d_s}=\frac{s_{H_2O}}{s_{MOH}}=\text{constant} \quad \text{when the base MOH is difficultly soluble}
\end{aligned}\right\}(a)$$

$$\left.\begin{aligned}
&\frac{4\alpha^3}{(1-\alpha)v_m^2}\cdot\frac{d_A^2}{d_s}=\frac{s^2_{H_2O}}{K_{M(OH)_2}}=\text{constant} \quad \text{when the base M(OH)}_2\text{ is soluble}\\
&\text{or}\\
&\frac{4\alpha^2}{(1-\alpha)v_m}\cdot\frac{d_A^2}{d_s}=\frac{s^2_{H_2O}}{s_{M(OH)_2}}=\text{constant} \quad \text{when the base M(OH)}_2\text{ is difficultly soluble}
\end{aligned}\right\}(b)$$

and

$$\left.\begin{aligned}
&\frac{27\alpha^4}{(1-\alpha)v_m^3}\cdot\frac{d_A^3}{d_s}=\frac{s^3_{H_2O}}{K_{M(OH)_3}}=\text{constant} \quad \text{when the base M(OH)}_3\text{ is soluble}\\
&\text{or}\\
&\frac{27\alpha^3}{(1-\alpha)v_m^2}\cdot\frac{d_A^3}{d_s}=\frac{s^3_{H_2O}}{s_{M(OH)_3}}=\text{constant} \quad \text{when the base M(OH)}_3\text{ is difficultly soluble}
\end{aligned}\right\}(c)$$

In other words, *the hydrolytic dissociation which is caused primarily by the formation of base can be calculated from a constant value found from the ionic product of water, and either the ionization constant or the solubility product of the base which is the cause of the hydrolytic dissociation.*

It will be observed that the variation of the hydrolytic dissociation with the dilution depends upon whether the base causing it is difficultly soluble or not. Thus *when 1 mole of salt reacts with 1 mole of water,* (*a*), *if the base is difficultly soluble, the extent of hydrolysis is independent of the dilution of the salt, while when the base is soluble the extent of hydrolysis depends upon the dilution.* It must be remembered here, however, that even when the salt is difficultly soluble, the hydrolytic dissociation and its relation to dilution will be the same as for a soluble base up to the value that would cause a *separation of solid base.*

When the hydrolysis is small, i.e., $1-\alpha$ is practically 1, and d_A and d_s are also equal to 1, it will be seen that for (*a*), (*b*), and (*c*), *for a soluble base,* the hydrolytic dissociation will vary as the $\sqrt{v_m}$, $\sqrt[3]{v_m{}^2}$, and $\sqrt[4]{v_m{}^3}$; while when the base is difficultly soluble the hydrolysis will be independent of the dilution for (*a*) and will vary as $\sqrt{v_m}$ and $\sqrt[3]{v_m{}^2}$ for (*b*) and (*c*).

CASE II. *The formation of un-ionized, or insoluble, acid is the direct cause of the hydrolytic dissociation, and the base formed is largely ionized.* Here, by definition, hydrolysis, which may occur in one of the three forms (*a*), (*b*), and (*c*), already mentioned, according as the positive ion of the salt is mono-, di-, or trivalent, must in *all* cases occur when the product, *in the solution* (since the acid in all three cases was taken as monobasic) $c_{A^-} \times c_{H^+}$, is greater than that which can exist in the absence of un-ionized acid, for then un-ionized acid must form. And the formation of acid (and base) must continue until the condition,

$$\text{final } c_{A^-} \times \text{final } c_{H^+} = K_{HA} \times c_{HA} \text{ formed}$$

is fulfilled. Or until the condition, when the acid is difficultly soluble,

$$\text{final } c_{A^-} \times \text{final } c_{H^+} = s_{HA}$$

is fulfilled. In all these cases, as will be noted, the acid is, or behaves as, a monobasic acid.

Since the final c_{H^+} is equal to $\frac{s_{H_2O}}{\text{final } c_{OH^-}}$, when d_B is the ionization of the amount of base formed, α is the percentage of hydrolytic dissociation, and d_s is the ionization of the salt left, we have, as before,

$$\text{final } c_{A^-} = \frac{d_s(1-\alpha)}{v_m} \left(\text{or } \frac{2d_s(1-a)}{v_m}, \quad \text{or} \quad \frac{3d_s(1-\alpha)}{v_m}\right),$$

$$\text{final } c_{OH^-} = d_B\frac{\alpha}{v_m} \left(\text{or } \frac{2d_B\alpha}{v_m}, \quad \text{or} \quad \frac{3d_B\alpha}{v_m}\right),$$

and $$\text{final } c_{HA} = \frac{\alpha}{v_m} \left(\text{or } \frac{2\alpha}{v_m}, \quad \text{or} \quad \frac{3\alpha}{v_m}\right).$$

The conditions for (*a*), (*b*), and (*c*), when the acid is soluble are therefore,

$$\frac{d_s(1-\alpha)}{v_m} \frac{s_{H_2O}}{d_B\frac{\alpha}{v_m}} = K_{HA} \times \frac{\alpha}{v_m},$$

$$2\frac{d_s(1-\alpha)}{v_m} \frac{s_{H_2O}}{\frac{2d_B.\alpha}{v_m}} = K_{HA} \times \frac{2\alpha}{v_m},$$

or

$$3\frac{d_s(1-\alpha)}{v_m} \frac{s_{H_2O}}{\frac{3d_B\alpha}{v_m}} = K_{HA} \times \frac{3\alpha}{v_m},$$

respectively; and when the acid is difficultly soluble and its solubility product is s_{HA},

$$\frac{d_s(1-\alpha)}{v_m}\,\frac{s_{H_2O}}{\frac{d_B\alpha}{v_m}}=s_{HA},$$

$$2\frac{d_s(1-\alpha)}{v_m}\,\frac{s_{H_2O}}{\frac{2d_B\alpha}{v_m}}=s_{HA},$$

or

$$3\frac{d_s(1-\alpha)}{v_m}\,\frac{s_{H_2O}}{\frac{3d_B\alpha}{v_m}}=s_{HA}.$$

These by simplification become, for a soluble, but slightly ionized, monobasic acid,

(*a*) $$\frac{a^2}{(1-\alpha)v_m}\cdot\frac{d_B}{d_s}=\frac{s_{H_2O}}{K_{HA}}=\text{constant},$$

(*b*) $$\frac{2\alpha^2}{(1-\alpha)v_m}\cdot\frac{d_B}{d_s}=\frac{s_{H_2O}}{K_{HA}}=\text{constant},$$

and

(*c*) $$\frac{3\alpha^2}{(1-\alpha)v_m}\cdot\frac{d_B}{d_s}=\frac{s_{H_2O}}{K_{HA}}=\text{constant};$$

and for *difficultly soluble monobasic acids* in all three cases

$$\frac{\alpha}{1-\alpha}\cdot\frac{d_B}{d_s}=\frac{s_{H_2O}}{s_{HA}}=\text{constant},$$

where in all three cases the extent of the hydrolytic dissociation is independent of the dilution of the salt.

In case the reaction is $M_2A+2H_2O=2MOH+H_2A$, where the dibasic acid H_2A is but slightly ionized into $2H^+$ and $A^=$ or but slightly soluble, and MOH is largely ionized, we find

$$\frac{d_s(1-\alpha)}{v_m}\left(\frac{s_{H_2O}}{2d_B\frac{\alpha}{v_m}}\right)^2 = K_{H_2A}\frac{\alpha}{v_m}$$

or

$$\frac{4\alpha^3}{(1-\alpha)v_m^2}\cdot\frac{d_B^2}{d_s} = \frac{s^2_{H_2O}}{K_{H_2A}} = \text{constant},\quad \text{for a soluble acid, and}$$

$$\frac{d_s(1-\alpha)}{v_m}\left(\frac{s_{H_2O}}{2d_B\frac{\alpha}{v_m}}\right)^2 = s_{H_2A};\ \text{ or }\ \frac{4\alpha^2}{(1-a)v_m}\cdot\frac{d_B^2}{d_s} = \frac{s^2_{H_2O}}{s_{H_2A}} = \text{constant},$$

for a difficultly soluble acid.

The same form of conclusion may be drawn here, naturally, as that on page 356, where the base caused the hydrolytic dissociation.

Case III. *The formation of both un-ionized acid and un-ionized base causes the hydrolytic dissociation; both are but slightly ionized.* This case falls under one or the other of those above, according as the base or acid has the smaller ionization constant. Although the mechanism of the reaction is the same here as above, the final result is quite different.

Assume that K_{HA} is smaller than K_{MOH}. Here the final c_{OH^-} is equal to $\frac{K_{MOH}c_{MOH}}{c_{M^+}}$, and since both MOH and HA are slightly ionized we shall have, practically, $c_{MOH} = c_{HA} = \frac{\alpha}{v_m}$ and, therefore, $c_{M^+} = c_{A^-} = \frac{d_s(1-\alpha)}{v_m}$. Consequently just as with (*a*); Case II, we must have

$$\frac{d_s(1-\alpha)}{v_m}\cdot\frac{s_{H_2O}}{\dfrac{K_{MOH}\frac{\alpha}{v_m}}{\frac{d_s(1-\alpha)}{v_m}}} = K_{HA}\times\frac{\alpha}{v_m},$$

which when simplified, after grouping the constants together gives

$$\frac{\alpha^2}{(1-\alpha)^2}\cdot\frac{1}{d_s{}^2}=\frac{s_{H_2O}}{K_{HA}\times K_{MOH}}=\text{constant},$$

the hydrolytic dissociation of a salt reacting with 1 mole of water, to form a slightly ionized acid and a slightly ionized base, is independent of the dilution, so long as the salt produced is completely ionized; and the constant of hydrolytic dissociation is equal to the ionic product for water, divided by the product of the ionization constants of the acid and base.

When the salt reacts with 2 or more moles of water the hydrolytic dissociation is also independent of the dilution, so long as the salt is completely ionized.

Thus for the reaction $MA_2+2H_2O \rightleftarrows M(OH)_2+2HA$, we find

$$\frac{d_s(1-\alpha)}{v_m}\left\{\frac{\dfrac{s_{H_2O}}{2K_{HA}\dfrac{\alpha}{v_m}}}{d_s\dfrac{1-\alpha}{v_m}}\right\}^2=K_{M(OH)_2}\frac{\alpha}{v_m},$$

from which it follows that

$$\frac{4\alpha^3}{(1-\alpha)^3}\cdot\frac{1}{d_s{}^3}=\frac{s^2{}_{H_2O}}{K^2{}_{HA}\times K_{M(OH)_2}}=\text{constant};$$

and for other forms of the reaction it may also be found without difficulty.

In both cases here the reaction (acid or alkaline) of the final equilibrium will depend upon the relative values of the terms K_{MOH} and K_{HA}. In the case of ammonium acetate, for example, since NH_4OH ($K=0.000023$) has a larger constant than acetic acid ($K=0.000018$), it is evident that the concentration of OH^- ion will be slightly greater than that of H^+, and the solution should be slightly alkaline.

Here it is not difficult to see that if both base and acid are difficultly soluble, the reaction will be complete at all dilutions, and the same result will be obtained if one is insoluble and the other but slightly ionized. The latter case is to be observed in the well-known basic acetate separation, where the ferric hydroxide is difficultly soluble and the already small ionization of the acetic acid formed is depressed by the presence of sodium acetate.

It is not only in the above general way, however, that we can find these final expressions which correlate the various concentrations coexisting in equilibrium as the result of a hydrolytic reaction, and those showing the variation of the extent of the hydrolysis of a salt with its varying dilution. For, without separating the possible processes into three general groups as we have done, we can simply consider all hydrolytic reactions together, and find in known terms for any one case the concentrations of H^+ and OH^- ions finally present in the equilibrium; and then substitute these in every case in the one fundamental equation

$$c_{H^+} \times c_{OH^-} = s_{H_2O},$$

and rearrange the result as we did above.

For example, let us consider the third case above, where both the base and the acid formed are but slightly ionized; in other words give constants according to the law of mass action. From the equations $c_{M^+} \times c_{OH^-} = K_{MOH} c_{MOH}$, and $c_{H^+} \times c_{A^-} = K_{HA} c_{HA}$, we find $c_{OH^-} = \frac{K_{MOH} c_{MOH}}{c_{M^+}}$ and $c_{H^+} = \frac{K_{HA} c_{HA}}{c_{A^-}}$. But since, both acid and base are slightly ionized, practically equal amounts of base and acid will form in the un-ionized state from the hydrolysis, i.e., $c_{MOH} = c_{HA} = \frac{\alpha}{v_m}$. Further, since if this be true, the amount of free M^+ ion left must be practically identical with that of free A^- ion left, we have

$c_{M+} = c_{A-} = \frac{d_s(1-\alpha)}{v_m}$. We have, then, substituting these values of c_{H+} and c_{OH-} in the s_{H_2O} equation,

$$\left(\frac{K_{MOH}\frac{\alpha}{v_m}}{\frac{d_s(1-\alpha)}{v_m}}\right)\left(\frac{K_{HA}\frac{\alpha}{v_m}}{d_s\left(\frac{1-\alpha}{v_m}\right)}\right) = s_{H_2O},$$

from which it follows that

$$\frac{\alpha^2}{(1-\alpha)^2}\cdot\frac{1}{d_s^2} = \frac{s_{H_2O}}{K_{MOH}\times K_{HA}} = \text{constant}.$$

In Case I(c) above, in a similar way, we would have, the base being soluble, but only slightly ionized,

$$c^3_{OH-} = \frac{K_{M(OH)_3}c_{M(OH)_3}}{c_{M+++}} \quad \text{or} \quad c_{OH-} = \sqrt[3]{\frac{K_{M(OH)_3}c_{M(OH)_3}}{c_{M+++}}},$$

where $c_{M(OH)_3}$, by definition, is equal to $\frac{\alpha}{v_m}$, and $c_{M+++} = \frac{d_s(1-\alpha)}{v_m}$, while $c_{H+} = 3d_A\frac{\alpha}{v_m}$. Substituting these in the s_{H_2O} equation, we find

$$\sqrt[3]{\frac{K_{M(OH)_3}\frac{\alpha}{v_m}}{d_s\left(\frac{1-\alpha}{v_m}\right)}} \times 3d_A\frac{\alpha}{v_m} = s_{H_2O},$$

or

$$\frac{K_{M(OH)_3}\frac{\alpha}{v_m}}{\frac{d_s(1-\alpha)}{v_m}} \times 27d_A{}^3\frac{\alpha^3}{v_m{}^3} = s^3_{H_2O},$$

from which it follows that

$$\frac{27\alpha^4}{(1-\alpha)v_m{}^3}\cdot\frac{d_A{}^3}{d_s} = \frac{s^3_{H_2O}}{K_{M(OH)_3}} = \text{constant}.$$

Perhaps this method in general is to be preferred to the other, because it is somewhat simpler and uses as the principal relationship the well-proven equation for the ionic product for water, employing the others simply as a means of determining the individual, constituent, terms.

It will be seen from the above that granting the law of mass action to be true in any one case it is a simple matter to find an expression for the equilibrium that will ultimately be established as the result of a hydrolytic reaction. Naturally, in practice, here, the presence of intermediate ions in any one case would prevent these laws being applied; where no such complication interferes, however, there is no reason why experiment should not agree with the calculated results.

In general the first form of expression derived is the more valuable for many purposes, though the latter form, equated to "constant," is useful as connecting directly the degree of hydrolytic dissociation and the dilution of the salt solution. The reader is advised to pay especial attention to the first form throughout, and especially to its very simple and logical derivation, for from that, if necessary, he can always derive the second form, instead of attempting to burden his memory with it.

Naturally, just as on pages 282 and 318, so long as d_s, d_A, or d_B, are equal to 1, we may define the hydrolytic constant ("constant"), for a reaction involving 1 mole of water, as equal to 1/2 the concentration in moles per liter at which the salt is 50% hydrolyzed. And it is also evident that knowing the constant for hydrolytic dissociation, we can calculate the degree of hydrolysis for any dilution, so long as the values of d_s, d_B, or d_A are known.

From the hydrolytic dissociation, determined according to the methods given later, it is of course possible for us to calculate the ionization constant or solubility product of the acid or base causing it, or when that is already known, to calculate the ionic product of water.

For example let us find the ionic product of water at 25°. A 0.1 molar solution of sodium acetate is 0.008% hydrolyzed. Here we may regard the sodium acetate as practically completely ionized, as will also be the sodium hydroxide formed, and we know that the constant of ionization of acetic acid at 25° is 0.000018. It is evident here, from the reaction

$$CH_3COO^- + Na^+ + H_2O \\ = Na^+ + xOH^- + (1-x)CH_3COO^- + xCH_3COOH,$$

where $x = 0.1 \times 0.0008$, that

$c_{CH_3COOH} = c_{OH^-} = 0.00008 \times 0.1 = 0.000008$ mole per liter at equilibrium, and since

$$c_{CH_3COO^-} = 0.1 - (0.00008 \times 0.1) = 0.1, \text{ practically},$$

and

$$0.000018 \times c_{CH_3COOH} = c_{H^+} \times c_{CH_3COO^-},$$

$$c_{H^+} = \frac{0.000018 \times 0.000008}{0.1} = 1.44 \times 10^{-9},$$

and

$$1.44 \times 10^{-9} \times 0.000008 = c_{H^+} \times c_{OH^-} = 1.15 \times 10^{-14},$$

i.e., the ionization of water (where $H^+ = OH^-$) is such that $H^+ = OH^- = \sqrt{1.15 \times 10^{-14}} = 1.07 \times 10^{-7}$ at 25°.

This value of s_{H_2O} could also be calculated directly by the substitution of $\alpha = 0.00008$ in the equation

$$\frac{\alpha^2}{(1-\alpha)10} = \frac{s_{H_2O}}{0.000018} = \text{constant};$$

from which, $s_{H_2O} = 1.15 \times 10^{-14}$

What is the hydrolysis of a 0.1 molar solution of potassium cyanide (assuming $d_s = d_B = 1$)? K for HCN is 13×10^{-10}, and $s_{H_2O} = (0.91 \times 10^{-7})^2$ at 25°.

$$\text{Constant} = \frac{\alpha^2}{(1-\alpha)v_m} = \frac{s_{H_2O}}{K_{HCN}} = \frac{(0.91\times10^{-7})^2}{13\times10^{-10}},$$

from which, since $v_m = 10$, we find $\alpha = 0.00798$; i.e., KCN$n/10$ is 0.8% hydrolyzed, forming OH^- ion and un-ionized HCN.

It will be noted in all cases of hydrolytic dissociation that since the ionization of water *increases* with increased temperature, up to a certain point, page 347, and the ionization of dissolved substances *decreases* with increased temperature, *the degree of hydrolytic dissociation increases with the temperature.* Thus for acetic acid, $K_{18°} = 18.3\times10^{-6}$, $K_{100°} = 11.4\times10^{-6}$, $K_{156°} = 5.6\times10^{-6}$, and $K_{218°} = 1.9\times10^{-6}$, while for ammonium hydrate $K_{18°} = 17.1\times10^{-6}$, $K_{100°} = 14\times10^{-6}$ and $K_{156°} = 6.6\times10^{-6}$. Comparison of these with the values s_{H_2O} for the various temperatures (page 348) shows that the hydrolysis of ammonium acetate (Case III) must increase decidedly with the temperature. And the same is true for all other cases.

In the table below are given the values of $\frac{\alpha^2}{(1-\alpha)v_m}$ for various equilibria in which but 1 mole of water reacts with the substance, the base causing the hydrolysis (Case I).

HYDROLYSIS OF HYDROCHLORIDES AT 25°

Base.	Per Cent Hydrolysis at $v_m = 32$.	$\frac{\alpha^2}{(1-a).m}$	Ionization Constant of Free Base.
Aniline	2.7	2.25×10^{-5}	5.3×10^{-10}
o-Toluidine	7.0	1.62×10^{-4}	7.3×10^{-11}
m- "	3.6	4.10×10^{-5}	2.9×10^{-10}
p- "	1.8	1.05×10^{-5}	1.13×10^{-9}
o-Nitroaniline	98.6	2.1	5.6×10^{-15}
m- "	26.6	3.01×10^{-3}	4.0×10^{-12}
p- "	79.6	9.58×10^{-2}	1.24×10^{-13}
Aminoazobenzene	18.1	1.25×10^{-3}	9.5×10^{-10}
Urea	....	0.781	1.5×10^{-14}

An example of Case I, where the salt reacts with 2 moles of water, is the hydrolysis of aluminum chloride according to the reaction,

$$AlCl_3 + 2H_2O \rightleftarrows Al(OH)_2Cl + 2HCl.$$

This has been investigated by Kullgren (Om metallsalters hydrolys, page 108. Dissertation. Stockholm, 1904). The following results will show how well this equilibrium follows the above law, and how it is possible to find the ionization constant by aid of the hydrolytic dissociation, knowing the ionic product for water at that temperature.

HYDROLYSIS OF $AlCl_3$ AT 100° C.

$$AlCl_3 + 2H_2O \rightleftarrows Al(OH)_2Cl + 2H^+ + 2Cl^-$$

v_m	α	d_A	d_s	$\frac{\alpha^3}{(1-\alpha)v_m^2}$	$\frac{\text{Constant}}{4} = \frac{\alpha^3}{(1-\alpha)v_m^2} \cdot \frac{d_A^2}{d_s}$
96	0.1488	0.966	0.76	420×10^{-9}	516×10^{-9}
384	0.3629	0.977	0.85	509×10^{-9}	571×10^{-9}
1536	0.7142	1	0.91	541×10^{-9}	594×10^{-9}
					Average, $\frac{\text{Constant}}{4} = 560 \times 10^{-9}$

The concentrations of base in the three cases are 0.00155, 0.000945 and 0.000465, respectively, the acid concentrations being twice these values. The average value of $\frac{\text{constant}}{4}$ in the last column may be used to determine $K_{Al(OH)_2Cl}$, for

$$\text{constant} = \frac{s^2_{H_2O}}{K_{Al(OH)_2Cl}} = 4\frac{\alpha^3}{(1-\alpha)v_m^2} \cdot \frac{d_A^2}{d_s}.$$

We obtain in this way (according to Kullgren) the value $K_{Al(OH)_2Cl} = 2.33 \times 10^{-19}$, where the ionization, presumably, gives $AlCl^{++}$ and $2OH^-$.

$Tl(NO_3)_3$, according to Spencer and Abegg (Zeit. f. anorg. Chem., 44, 397, 1905), seems to react directly with 3 moles of water, $Tl(OH)_3$ having a solubility equal to $10^{-13.58}$ moles per liter, i.e., $s = 10^{-52.896}$ and so is also an illustration of Case I, where the formation of insoluble $M(OH)_3$ is the primary cause of the hydrolysis. Unfortunately the actual degrees of hydrolysis have not been determined, but simply the fact that the reaction goes in this way.

Examples of Case II, where the hydrolytic dissociation is due primarily to the acid are the hydrolysis of potassium cyanide, sodium acetate, sodium carbonate, the barium salt of hydroxyazobenzene, etc.

PERCENTAGE OF HYDROLYSIS

v_m	t	%	Constant
Ba Salt of Hydroxyazobenzene			
50	25°	1.10	24×10^{-7}
Sodium Acetate			
548	156°	0.87	—
593	218°	4.34	—
118	218°	1.12	—
15.6	218°	0.29	—
10	25°	0.008	—
Sodium Carbonate			
5	25°	2.12	—
10	25°	3.17	—
20	25°	4.87	—
40	25°	7.10	—
Potassium Phenate			
10	25°	3.05	—
50	71°	6.65	—
Borax			
32	25°	0.92	—

For results on sodium borate, see Lundberg, Zeit. f. phys. Chem., 64, 442–448.

Examples of Case III, which have been studied, where both acid and base are but slightly ionized, and α is independent of the dilution, so long as the ionization of the salt is complete, are solutions of ammonium acetate, ammonium borate, aniline acetate, etc.

Aniline Acetate

v_m	t	α	d_s	Constant $=\left(\frac{\alpha}{1-\alpha}\cdot\frac{1}{d_s}\right)^2=\frac{s_{H_2O}}{K_{HA}K_{MOH}}$
39.32	15°	0.457	0.869	—
195.9		0.468	0.95	—
39.32	25°	0.513	0.873	—
195.9		0.523	0.953	—
39.32	40°	0.590	0.878	—
195.9		0.595	0.959	—
Ammonium Borate				
46.46	15°	0.390	0.880	0.528
92.92		0.394	0.944	0.508
46.46	25°	0.458	0.885	0.912
92.92		0.462	0.919	0.875
46.46	40°	0.556	0.894	1.961
92.92		0.560	0.956	1.883
Ammonium Acetate				
401	100°	0.046	—	—
100	100°	0.048	—	—
42.3	156°	0.1797	—	—
105.6	156°	0.1860	—	—
83.3	218°	0.526	—	—
166.6	218°	0.532	—	—
33.3	306°	0.913	—	—
100.0	306°	0.915	—	—

We must now consider, very briefly, the methods by which the degree of hydrolytic dissociation can be experimentally determined. It is obvious from what has already been said, that the determination of the concentration of any one of the reacting constituents, if we know the chemical reaction taking place, will give us a complete view of the equilibrium.

The general methods so far used for this purpose are as follows:

The free acid (H^+) or free base (OH^-) is measured by observations of the velocity of the inversion of sugar at 100°, or the hydrolysis of esters, respectively, as was described above, pages 304 and 308 (Walker, Zeit. f. phys. Chem., 4, 319, 1889; Shields, *ibid.*, 12, 167, 1893; Kullgren, *ibid.*, 85, 466–480, 1913).

The determination of the ionized portion by means of conductivity observations (see Chapter IX).

For details as to this method see Ley (Zeit. f. phys. Chem., 30, 193, 1899), Goodwin, *ibid.*, 21, 1, 1896, Kullgren (l. c.), Lundén, (Jour. Chim. Phys., 5, 145, and 574, 1907) and Noyes (Carnegie Pub. No. 63, 1907).

When one of the active constituents is colored, the reaction may also be followed by aid of spectro-photometric observations, as shown by Moore (Phys. Rev., 12, 151–176, 1900), but, naturally, this method is much limited in its applicability.

Other methods are based on the determination of the concentration of H^+ by electromotive force measurements, employing the hydrogen electrode (Denham, Trans. Chem. Soc., 93, 41, 1908); on the mobility of the ions (Denison and Steele, Trans. Chem. Soc., 89–90, 999, 1368, 1906); on the distillation of systems where the hydrolysis is due to a volatile constituent (Veley, Trans. Chem. Soc., 87, 29, 1905; Hill, *ibid.*, 90, 1273, 1906; Naumann and Rücker, J. f. prakt. Chem,. 74, 249, 1906; and Naumann and Müller, *ibid.*, 74, 218, 1906).

One method, which can be used for salts of weak acids with strong bases, or salts of weak bases with strong acids, has been suggested by Farmer (Trans. Chem. Soc., 79, 863, 1901, and *ibid.*, 85, 1713, 1904), which, owing to the importance of the principle involved, is briefly considered below. The method is based upon the coefficient of distribution of a substance between water and another solvent, ether (page 291).

Let the coefficient of partition of the distributable base (of the same molecular weight in both solvents), for example, between water and ether, be constant $=\frac{w_w}{w_e}$, where w_w and w_e are the weights of the base *in grams per cc.* of the layers, water and ether, at equilibrium. After thus determining the "constant," by experiment, we are to use it to find the concentration in moles per liter in the water layer, and consequently must proceed as follows: Assume the reaction

$$MA+H_2O \rightleftarrows MOH+HA,$$

where the base is very slightly ionized and soluble in both solvents, while the salt and acid are practically completely ionized and soluble only in the water layer. It is evident, from constant $=\frac{w_w}{w_e}$, that $w_w=\text{constant}\times w_e$.

The *moles of substance per liter of water*, then, will be $1000\frac{w_w}{M}$ where M is the molecular weight of the substance in solution; or, substituting for w_w, its value above, we find

$$\text{Base, per liter of water,}=\frac{1000w_e\times\text{constant}}{M}\text{ moles.}$$

If the water layer measures 1000 cc., and the ether layer x cc., then the total moles of base in the two-layer system must be $\frac{1000\text{ constant}\times w_e}{M}+\frac{xw_e}{M}$. This, however, according to the above chemical reaction, must also be equal to the total acid in the system, which is contained only in the water layer. We have, then,

$$\text{Acid in water layer} = \frac{1000 \text{ constant} \times w_e}{M} + \frac{xw_e}{M} \text{ moles per liter,}$$

$$\text{Base in water layer} = c_w = \frac{1000 \text{ constant} \times w_e}{M}.$$

Salt, un-hydrolyzed, in water layer

$$= c - \left(\frac{1000 \text{ constant} \times w_e}{M} + \frac{xw_e}{M}\right),$$

where c is the original concentration in the water solution of the salt, and all are in moles per liter.

The hydrolytic constant (Constant) for the salt MA must be, therefore, since these three substances are in equilibrium in the water layer,

$$\text{Constant} = \frac{\text{acid} \times \text{base}}{\text{salt}}$$

$$= \frac{\left(\frac{1000 \text{ constant} \times w_e}{M} + \frac{xw_e}{M}\right)\left(\frac{1000 \text{ constant} \times w_e}{M}\right)}{c - \left(\frac{1000 \text{ constant} \times w_e}{M} + \frac{xw_e}{M}\right)},$$

and from this, knowing the dilution of the salt, v_m in $\frac{\alpha^2}{(1-\alpha)v_m} = \text{Constant}$, we can solve for α, the hydrolytic dissociation of the salt MA, in the equation

$$\alpha = \sqrt{\text{Constant } v_m + \frac{(\text{Constant})^2 \, v_m^2}{4}} - \frac{\text{Constant } v_m}{2}.$$

As an illustration of this method we may take the hydrolysis of aniline hydrochloride, where the hydrolysis is caused by the formation of free un-ionized aniline which distributes between the water and ether. After shaking (at 25°) 1 liter of water containing 0.09969 mole of aniline hydrochloride with 59 cc. of ether we find 0.001156 gram of aniline ($M=93$) per cc. of ether, i.e., $\frac{59\times 0.001156}{93}=0.000733$ mole of aniline in the 59 cc. of the ether layer. The amount of aniline in the 1000 cc. of the water layer, then, is $\frac{1000\frac{1}{10.1}\times 0.001156}{93}=0.00123$, for "constant" was previously found to be $\frac{1}{10.1}$, i.e., there is always at 25°, 10.1 times as much aniline in 1 cc. of the ether layer as in 1 cc. of the water layer. The total amount of free base in the *system* of the 1059 c.c., then, is, $0.00123+0.000733=0.00196$, and this is equal to the amount of free acid in the *water layer*, while the final un-hydrolyzed salt in the water layer is $0.09969-0.00196=0.09773$, for the original concentration salt was 0.09969 mole per liter. We have then in the water layer

$$\text{Constant}=\frac{0.00123\times 0.00196}{0.09773}=\frac{\alpha^2}{(1-\alpha)v_m}=0.0000247,$$

from which for this practically $m/10$ solution, the hydrolytic dissociation is,

$$\alpha=0.0156 \quad \text{or} \quad 1.56\%.$$

This method is also to be used when appropriately altered for reactions involving two or more moles of water; and is also applicable to those reactions producing un-ionized acid, where that is distributed between the two solvents (see Farmer,

l. c.). For a table showing the hydrolytic dissociation of the various salts thus far studied, see Landolt-Börnstein-Roth, 1912, pp. 1194-1198.

Determination of the ionization constant from observations of increased solubility.—A very ingenious and accurate method for the determination of the ionization constant of an acid or a base, from its increased solubility in a base, or an acid, with a known ionization constant, is given by Lowenherz (Zeit. f. phys. Chem., **15**, 385, 1898). Either the acid or base to be determined must be difficultly soluble in water, i.e., just those conditions are advantageous which in the usual methods are sources of trouble.

The general form of the equilibrium arising by the neutralization of an acid with a base may be written as follows:

$$HA+MOH \rightleftarrows a\mathrm{HA}+b\mathrm{MOH}+c\mathrm{H_2O}+d\mathrm{MA}+e\mathrm{H^+}+f\mathrm{A^-}+g\mathrm{M^+}+h\mathrm{OH^-}.$$

Calling the total amount of acid present ΣA, and the total base ΣM, we have the following conditions existing at equilibrium:

(1) $A^- = \Sigma A - HA - MA.$

(2) $A^- = M^+ + H^+ - OH^-$. The sum of the positive ion concentrations is equal to the sum of the negative, for all solutions must be electrically neutral.

(3) $$M^+ = \Sigma M - MA - MOH.$$

(4) $$M^+ = A^- + OH^- - H^+.$$

(5) $$H^+ = \frac{K_{\mathrm{acid}}HA}{A^-}.$$

(6) $$H^+ = \frac{S_{H_2O}}{OH^-}.$$

(7) $$OH^- = \frac{K_{\mathrm{base}}MOH}{M^+}.$$

(8) $$OH^- = \frac{S_{H_2O}}{H^+}.$$

(9) $$MA = (1 - \alpha_{MA}) \text{ total } MA.$$

(10) $$MOH = (1 - \alpha_{MOH}) \text{ total } MOH.$$

(10*a*) MOH, when difficultly soluble, is the same as in a saturated water solution.

(11) $$H_2O = \text{total } MA.$$

(12) $$HA = (1 - \alpha_{HA}) \text{ total } HA.$$

(12*a*) HA, when difficultly soluble, is the same as in a saturated water solution.

The solubility of a difficultly soluble acid, for example, will be greater in a solution of a base than in pure water, for the reaction causes the removal of H^+ ions from the acid, and this necessitates the further ionization of the un-ionized portion, and the solution of more solid. The difference in solubility in the base and in water gives directly the amount of water formed, for that amount is the cause of the reaction which increases the solubility. The total salt formed is also equal to this difference, but this, unlike the water formed, may be, and usually is, ionized.

The sequence in which the equations above may be used in any individual case depends entirely upon the nature of the equilibrium. *The first thing in all cases is to find the amount of salt formed and, from its ionization in this dilution, the concentration of its un-ionized portion.* The following very simple examples will probably best show the principles involved in such calculations.

Assume we have an acid, soluble to 0.001 mole per liter, the constant of ionization of which is unknown, which is soluble to 0.003 mole per liter in a 0.1 molar solution of the base MOH. The base is 90% ionized, and the salt which is formed has a value of α equal to 0.98 at this dilution. What is the constant of ionization of the acid?

Here we must find $K_{HA} = \frac{c_{H^+} \times c_{A^-}}{c_{HA}}$. Since the difference in the two solubilities is 0.002, the amount of water and the total salt formed are each equal to 0.002 mole per liter. We have, then,

$$\begin{aligned}
MA &= (1-\alpha)\ (\text{total } MA)\\
&= (1-0.98)(0.002).\\
M^+ &= M^+ \text{ of } MOH - \text{loss of } M^+ \text{ as } MA\\
&= 0.9(0.1) - (0.002)(1-0.98).\\
OH^- &= OH^- \text{ of } MOH - \text{loss of } OH^- \text{ as } H_2O\\
&= 0.9(0.1) - (0.002).\\
H^+ &= \frac{S_{H_2O}}{OH^-}\\
&= \frac{(1.09\times 10^{-7})^2}{0.9(0.1)-(0.002)}.\\
A^- &= H^+ + M^+ - OH^-\\
&= \frac{(1.09\times 10^{-7})^2}{0.9(0.1)-(0.002)} + [0.9(0.1)-(0.002)(1-0.98)]\\
&\qquad -[0.9(0.1)-(.002)]\\
&= \frac{(1.09\times 10^{-7})^2}{0.088} + 0.00196.\\
HA &= \Sigma A - A^- - MA\\
&= 0.003 - \left[\frac{(1.09\times 10^{-7})^2}{0.088} + 0.00196\right]\\
&\qquad -(1-0.98)(0.002).
\end{aligned}$$

And since

$$K = \frac{c_{H^+} \times c_{A^-}}{c_{HA}},$$

we can evaluate it by substituting the last three values given above, i.e., those for H^+, A^-, and HA.

Proceeding in this way, and only in this way, we can find the concentrations of the various constituents at equilibrium.

The sequence of calculation is somewhat different when the base is difficultly soluble and K_{base} is unknown, an acid solution with a known degree of ionization serving as solvent.

Assume a base, which is soluble to 0.001 mole per liter, to be soluble in a 0.1 molar solution of acid ($\alpha=0.90$) to the extent 0.003 mole per liter, the salt being ionized to 0.98%. What is $K\left(=\frac{c_{M^+}\times c_{OH^-}}{c_{MOH}}\right)$ for the base?

Here again

$$MA=(0.002)(1-0.98),$$

but now we must first determine A^- instead of M^+, as above, i.e.,

$$\begin{aligned}A^- &= A^- \text{ of HA} - \text{loss of A as MA}\\ &=0.9(0.1)-(0.002)(1-0.98).\\ H^+ &= H^+ \text{ of HA} - \text{loss of } H^+ \text{ as } H_2O\\ &=0.9(0.1)-(0.002).\\ OH^- &= \frac{S_{H_2O}}{H^+}\\ &=\frac{(1.09\times10^{-7})^2}{0.9(0.1)-(0.002)}.\\ M^+ &= A^- + OH^- - H^+\\ &=[0.9(0.1)-(0.002)(1-0.98)]+\frac{(1.09\times10^{-7})^2}{0.9(0.1)-(0.002)}\\ &\quad-[0.9(0.1)-(0.002)].\\ &=0.00196+\frac{(1.09\times10^{-7})^2}{0.088}.\end{aligned}$$

$$\mathrm{MOH} = \Sigma M - \mathrm{M}^+ - \mathrm{MA}$$

$$0.003 - \left[0.00196 + \frac{(1.09 \times 10^{-7})^2}{0.088}\right] - (0.002)(1 - 0.98)$$

and

$$K_{\text{base}} = \frac{c_{\mathrm{M}^+} \times c_{\mathrm{OH}^-}}{c_{\mathrm{MOH}}},$$

the values of which are above, viz., M^+, OH^-, and MOH.

In case the acid is dibasic, or the metal of the base is divalent, the appropriate changes may be made in the above formulas without difficulty.

In all cases, however, it is necessary to have the solvent (acid or base) considerably more concentrated than the dissolved substance (base or acid).

Other ionic equilibria.—In order that the importance of the things we have studied in the sections above may be more clearly realized, we shall now consider very briefly their application to a few other questions of general chemical interest. Since the states of equilibrium which we most often encounter in our daily experience are those composed of ionized substances, and since those composed of un-ionized substances are comparatively simple and easy to determine, we shall restrict ourselves here to the consideration of systems containing ionized substances.

The simpler cases of ionic equilibria, i.e., those existing in simple electrolytes, have already been considered above. We found there that the law of mass action enables us to foresee the equilibrium in systems composed of organic acids or bases, of substances which are difficultly soluble, or of those of which the ionization is very slight. But for other systems, characterized by a large degree of ionization, the law of mass action is apparently inapplicable, and must be replaced by certain empirical relations.

We also found complications to arise in these equilibria, produced by the further dissociation at higher dilutions of one of the two ions observed at lower dilutions. This is the case with the poly-basic organic acids, which, up to the dilution at which $\alpha = 0.5$, behave as though monobasic, only showing their real basicity above this dilution. Even in such a case, however, the process can be followed or foreseen by the law of mass action, each form of ionization leading to a constant ratio of the concentrations of the constituents. An analogous case with a strong electrolyte is that of sulphuric acid, which ionizes in two stages, as follows:

$$H_2SO_4 = H^+ + HSO_4,$$

$$HSO_4^- = H^+ + SO_4^=.$$

Here, however, we cannot follow the process by the law of mass action, and the first stage is only to be observed in concentrated solutions. Indeed, at and above a dilution of 1 mole in 5 liters no trace of the HSO_4^- ion can be detected, and a dilution of 1 mole in 1000–2000 liters shows practically complete ionization into $2H^+$ and $SO_4^=$. The behavior of salts of the type of $BaCl_2$ is similar to this; and in general we may say that *the more dilute the solution the smaller the amount of a complex, intermediate, ion present.* (See Luther, Z. f. Elektrochem., 13, 294, 1907; and Noyes, Carnegie Publication, 239–281, No. 63.)

All these cases of equilibrium are comparatively simple, however, for all the ionized matter present arises from the one original substance with which we start. The cases we are now to consider, i.e., those equilibria resulting from the reaction of two or more substances, are somewhat more complicated experimentally, for the ionized matter may be due to several substances, but theoretically they are to be treated just as the others.

Before considering the specific cases of equilibrium which have been observed, it will be well to review very briefly the various methods for the determination of ionization and molecular weight in solution, in order that the physical-chemical analysis of such systems may be quite clear. In those electrolytes ionizing into two portions measurements of the electrical conductivity and the freezing-point depression give all the necessary information, i.e., of ionized, as well as of un-ionized matter. This is also true when three ions are formed completely. When one of the three ions is formed to a smaller extent than the others, however, as is the case with the second H^+ ion of dibasic organic acids, some other method, in addition to the ones above, must be employed in order to show its concentration. As the equilibrium becomes still more complicated, i.e., contains other ionized and un-ionized substances, still other methods must also be employed. In short, the physical-chemical analysis can only be accomplished by a combination of two or more of these methods.

Starting with a given solution containing various ions and un-ionized substances, by the application of all or some of the following methods, we can, of course, ascertain the concentration of each of the constituents if this be necessary. As a matter of fact, however, this is usually unnecessary, for, knowing the values of certain ones, those of the others may be calculated by aid of the chemical and physical-chemical relations.

The electrical conductivity of a solution gives directly *the total concentration of the ions which it contains;* while the freezing-point, boiling-point, vapor-pressure, or osmotic pressure give the *total number of moles per liter, i.e., of ionized plus un-ionized matter.* These are the general methods applicable to all kinds of ionized or un-ionized matter and their application to an unknown solution is obvious. In addition to these, however, there are certain other special methods, applicable to certain kinds of ions and un-ionized matter, which enable us to make a more detailed analysis of the solution. For example, by the depression of the solubility of a substance with an ion in common, the concentration of that ion in the solution employed as the solvent may be calculated, and with great accuracy. The *nature* of the ions in general may be determined by migration experiments, i.e., by observing the changes in concentration due to the passage of the electric current; and by aid of electromotive force measurements the individual *concentrations* of many kinds of ions may be accurately calculated. For details as to these methods see Chapter IX. Concentrations of ionized hydrogen may also be found from the speed of the inversion of cane sugar, using a weak, known solution of an acid as a standard; and OH^- ion can be determined from the speed of saponification of an ester, a known and weak solution of a strong base being used as a standard. And, finally, un-ionized aggregates can be determined by partition or distribution experiments, i.e., by finding the concentration of the substance in another, immiscible solvent, after this has been shaken with the original solution. And this, it is to be remembered, is not restricted to any one un-ionized substance, for even when several are present together they behave as if they were alone, and so can be determined, so long as the proper solvent is selected. For an illustration of the combination of above methods, see Morse, Zeit. f. phys. Chem., 41, 722, 1902.

By these methods, then, it is possible for us to find the concentrations of the various substances present at equilibrium, both ionized and un-ionized, and thus to define exactly the conditions necessary and sufficient for the retention of that state.

As was said above, we are now to consider the equilibria resulting from the reaction of two or more substances, but, since a chemical reaction in ionized systems depends largely upon the formation of un-ionized or difficultly soluble substances, it will be seen at once that the law of mass action is applicable to these systems. For such cases where it is inapplicable we have no guiding principle at present, but these are few, so far as we know, and at any rate are of lesser importance in ordinary work.

One of the first questions arising in qualitative analysis is—what occurs when the precipitation of $Mg(OH)_2$ by ammonium hydrate is prevented by the presence of ammonium chloride? The older theory of this influence assumed the formation of a complex salt $(MgCl_4)(NH_4)_2$, which is not decomposed by ammonium hydrate; while according to the new theory it is due to the fact that the ionization of the ammonium hydrate is so decreased by the presence of the NH_4^+ ion of the chloride that the solubility product of $Mg(OH)_2$ cannot be exceeded, and hence that is not formed.

This question was first investigated by Lovén (Zeit. f. anorg. Chem., **37**, 327, 1896). If the action is due to the driving back of the ionization of NH_4OH by the NH_4^+ of NH_4Cl, the reaction would be

$$MgCl_2 + 2NH_4OH \rightleftarrows Mg(OH)_2 + 2NH_4Cl.$$

And in every case, even when an excess of NH_4Cl is present, we must have the following relations at equilibrium:

$$c_{NH_4^+} \times c_{OH^-} = k_1 c_{NH_3},$$

$$c_{Mg^{++}} \times c^2_{OH^-} = s_{Mg(OH)_2},$$

or, by combination,

$$c_{Mg^{++}} \times \left[\frac{k_1 c_{NH_3}}{c_{NH_4^+}}\right]^2 = s_{Mg(OH)_2},$$

i.e., $$c_{Mg^{++}} \times \left[\frac{c_{NH_3}}{c_{NH_4^+}}\right]^2 = \frac{s_{Mg(OH)_2}}{k_1^2} = k, \text{ a constant.}$$

Lovén found the following concentrations at equilibrium, starting with different salts of magnesium and various concentrations of ammonia and ammonium chloride, the temperature being 16–17°.

Mg.	NH_3.	NH_4.	*k*.
0.0203	0.0421	0.01022	0.34
0.0281	0.02027	0.0059	0.33
0.03762	0.0189	0.00655	0.31
0.1084	0.0499	0.0286	0.33

Although in the calculation of the constant *k* the ionic concentrations of Mg and NH_4 should be used in the above, complete ionization of the Mg and NH_4 salts are assumed, and the total amounts employed. As will be seen, since these concentrations were determined by ordinary analytical methods, the value of *k* is constant within the experimental limits. Lovén's own formula was expressed somewhat differently, but this form is used here so that it may be in accord with other work of the same kind.

Herz and Muhs (Zeit. f. anorg. Chem., 38, 138, 1904) studied this same equilibrium, when attained from the other direction, i.e., according to the reaction

$$Mg(OH)_2 + 2NH_4Cl \rightleftarrows MgCl_2 + 2NH_4OH.$$

Here, just as above, we have

$$c_{NH_4^+} \times c_{OH^-} = k_1 c_{NH_3}$$

and

$$c_{Mg^{++}} \times c^2_{OH^-} = s_{Mg(OH)_2};$$

but, since no NH_4OH was added, we know that

$$c_{NH_3} = 2c_{Mg^{++}},$$

hence

$$c_{Mg^{++}}\left[\frac{2k_1c_{Mg^{++}}}{c_{NH_4^+}}\right]^2 = s_{Mg(OH)_2},$$

or

$$\frac{c^3_{Mg^{++}}}{c^2_{NH_4^+}} = \frac{s_{Mg(OH)_2}}{4k_1^2} = \text{constant},$$

i.e.,

$$\frac{c^{1.5}_{Mg^{++}}}{c_{NH_4^+}} = \text{constant}.$$

At 29° Herz and Muhs found the following results:

Mg.	NH_4^+.	Constant.
0.049	0.0771	0.141
0.0638	0.106	0.152
0.089	0.172	0.154
0.108	0.25	0.140
0.156	0.388	0.159

for ammonium chloride, while for ammonium nitrate they found

0.0495	0.076	0.145
0.0833	0.049	0.131

Here, also, the ionization is assumed to be complete, and it certainly is within a few per cent of being so. The values of the constants in the two investigations are not to be compared here, for unfortunately the temperatures differ which would probably exercise a great influence on the ammonium hydrate solution, as well as upon the solubility, and consequently the solubility product, of $Mg(OH)_2$.

In addition to these independent proofs that no complex is formed in such solutions we also have another based upon entirely different principles (Treadwell, Zeit. f. anorg. Chem., 37, 327, 1903). The molecular weight of a solution containing the chlorides of magnesium and ammonium in the ratio to form a complex salt, if it did exist, can be found from the following data:

A mixture of 0.1466 gram of $MgCl_2$, and 0.1647 gram of NH_4Cl (i.e., 1 mole of $MgCl_2$ to 2 of NH_4Cl) dissolved in 20 grams of water causes a depression of the freezing-point equal to 0°.9609. From this the average molecular weight of the substance in solution is found to be 29.97.

Assuming the salts to be present as a mixture, and that they are practically completely ionized (for the justification of which see below), the average molecular weight would be $\frac{202.32}{7} = 28.9$, for a mixture of 1 mole of $MgCl_2$ and 2 moles of NH_4Cl would dissociate into seven moles of ions. If a compound were formed there could not be more than three ions formed at most, and the minimum molecular weight in solution would be $\frac{202.32}{3} = 67.44$.

Solutions formed by each salt alone in this dilution give the following results:

0.1466 gram of $MgCl_2$ in 20 grams of water depresses the freezing-point 0.°3956, from which $M = 34.27$, instead of $\frac{MgCl_2}{3} = \frac{95.26}{3} = 31.75$.

And 0.1647 gram of NH_4Cl in 20 grams of H_2O gives a freezing-point depression of 0°.5511, i.e., $M = 27.75$, instead of $\frac{NH_4Cl}{2} = \frac{53.52}{2} = 26.74$.

These results show that the ionization of each alone at this dilution is nearly complete, and certainly the simultaneous solution cannot change the ionization enough to significantly change the result for the average molecular weight. If the two formed a compound, the value for the average molecular weight could not under any circumstances be as low as 29.97, as we find it. This example illustrates very well the difference between a complex salt and a simple mixture of two or more salts. In the former case the ionization is changed, i.e., a complex ion is formed; in the latter the ions formed are the same as those which exist when the substances are present alone in the solution.

The behavior of a mixture of $MnCl_2$ and NH_4Cl can be seen from the following results: 0.0968 gram $MnCl_2$ and 0.0824 gram NH_4Cl (i.e., 1 mole to 2) in 20 grams of H_2O give a depression of the freezing-point equal to 0°.4797, i.e., $M=34.56$. Assuming that the compound $[MnCl_4][NH_4]_2$ is ionized into three ions, it could not be more, the average molecular weight, just as above, would be $\frac{232.96}{3}=79.99$, while a simple mixture of the two salts, the ionization remaining unchanged, would lead to $\frac{232.9}{7}=33.28$.

We can conclude, then, that in such solutions, neither system forms a complex salt, and that the behavior of magnesium salts with ammonium hydrate simply depends upon the concentration of the OH^- ion present, and upon those ions which can alter the concentration of this.

One of the questions which gave much trouble before the inception of the electrolytic theory of dissociation was that in regard to the sequence of separation, when it is possible for two salts of differing solubility to be formed in a solution. According to the older theory it was assumed that the more insoluble one always formed first, and could be separated from the other by fractional precipitation. This, however, is found not to be in accord with the experimental facts, which, on the other hand, are perfectly represented by the law of mass action. This subject has been investigated by Findlay (Zeit. f. phys. Chem., 34, 409, 1900) in the case of the reversible reaction

$$\underset{\text{solid}}{PbSO_4}+\underset{\text{dissolved}}{2NaI}\rightleftarrows\underset{\text{solid}}{PbI_2}+\underset{\text{dissolved}}{Na_2SO_4}.$$

Applying the law of mass action to this, since at any one temperature the concentrations of the solids in solution are constant, we have

$$\frac{c^2_{\mathrm{I}^-}}{c_{\mathrm{SO}_4^-}}=\text{constant},$$

for the reaction may also be written

$$\underset{\text{solid}}{\mathrm{PbSO_4}}+2\mathrm{I}^- \rightleftarrows \underset{\text{solid}}{\mathrm{PbI_2}}+\mathrm{SO_4^=}.$$

By aid of analysis, and conductivity and electromotive force observations, Findlay found the ratio $\frac{c^2_{\mathrm{I}^-}}{c_{\mathrm{SO}_4^=}}$ to be a constant for all such systems, and to have a value at 25° lying between 0.25 and 0.3. The outcome of the investigation may be summed up as follows: *From a mixed solution of iodide and sodium sulphate, by the addition of a soluble lead salt, pure lead iodide* (*the more soluble*) *can be precipitated if the ratio of the square of the concentration of the iodine ion to the concentration of the sulphate ion is greater than the equilibrium constant. When the ratio becomes equal to this constant, both lead iodide and sulphate are precipitated together, the ratio* $\frac{c^2_{\mathrm{I}^-}}{c_{\mathrm{SO}_4^=}}$ *remaining constant. And all this is true for the sulphate when the ratio is smaller than the constant.*

It will be observed from these examples that by aid of the law of mass action, even though it fails to hold for strong electrolytes, we can foresee and regulate many, if not most, of the reactions with which we come in contact. Many other examples could be cited here to illustrate the methods of application, but the few above will suffice to bring out the general principles, and enable the reader to follow work of this sort. Interesting cases of ionic equilibria have also been studied by von Ende

(Dissertation Göttingen, 1899), Morse (Zeit. f. phys. Chem., 41, 709, 1902), Sherrill (Zeit. f. phys. Chem., 43, 705, 1903), Sherrill and Skowronski (J. Am. Chem. Soc., 27, 30, 1905), Noyes and Whitcomb (J. Am. Chem. Soc., 27, 747, 1905), Abel (Zeit. f. anorg. Chem., 26, 377, 1901), Knox (Zeit. f. Elektrochem., 12, 477, 1906), Bjerrum (Zeit. f. phys. Chem., 59, 336, 1907), Abegg and Spencer (Zeit. f. anorg. Chem., 46, 406, 1905), Haber and Le Rossignol (Ber., 40, 2144, 1907), Wells (J. phys. Chem., 10, 79, 1906), Weigel (Zeit. f. phys. Chem., 58, 293, 1907), and many others.

The color of solutions.—The color of a solution depends apparently upon the condition of the solute in the solvent. If a substance is not at all ionized, or but slightly so, any color it may possess must be attributed to the un-ionized substance. In case the ionization is practically complete the color of the solution will be the result of the mixture of the colors of the ions; or if only one is colored that color will be the color of the liquid. When partly dissociated, then, the color of a solution will be the result of the mixture of the colors of the ions and the un-ionized portion; or if only one of these is colored that color will be the color of the liquid. The un-ionized portion in cases, however, may also show the color of the ion; see Noyes, Technology Quarterly, 17, 306, 1904.

There is always a chance of error here if the color of the solid is assumed to be its color in solution. The color of a crystal, for example, is very often different from that of the substance in the form of powder, and, further, it is conceivable that an ionization takes place in the water of crystallization. In this latter case, of course, the solid would exhibit the same color as the colored ion. The only correct way to find the color of the undissociated portion in solution is to use a solvent in which the substance is not dissociated to any extent; then the color can be directly observed. This is not difficult to carry out, for all solvents have a different dissociating power, and either alcohol, ether, benzene, chloroform, or acetone will be found to serve the purpose.

The ions of most acids are colorless; consequently all salts of a metal in very dilute solutions will have the same color i.e., the color of the metallic ion. In more concentrated solutions this is not true, for many un-ionized substances are colored and, as they are now present to a greater amount, the color of the solution is the result of the mixture of these and the ions. An example of this is given by solutions of cuprous chloride, where the color of the un-ionized portion is yellow. But the copper ion is blue, hence the color of a solution of cuprous chloride may be either yellow, green, or blue, according as it is undissociated or ionized to a lesser or greater degree. All copper solutions when very dilute, provided the negative ion is colorless, show the same blue color.

The formation of a complex ion can be followed very closely when it is composed of a colored and a colorless ion. Thus if a KCN solution is added to a colored copper solution the color instantaneously disappears, due to the formation of the ion $CuCN_4^{=}$. The formation of a complex ion can be proven in this way, but its nature can only be shown by migration experiments, as was mentioned above. (See Chapter IX.)

CHAPTER IX

ELECTROCHEMISTRY

A. The Migration of the Ions *

Electrical units and Faraday's law.—The unit of electrical resistance is the *ohm*, i.e., the resistance at a temperature of 0° C. of a column of mercury 106.3 centimeters long, with a cross-section of 1 square millimeter. This is equal to 10^9 ergs.

The unit of current strength is that current that will separate 0.001118 gram of silver from a solution in one second, and is called the *ampere*—equal to 10^{-1} ergs.

The unit of electromotive force (E) is the *volt*, or 10^8 ergs. This unit is such that the standard Weston cell at 20° has a value $E=1.0183$ volts.

The unit of the quantity of electricity (Q) is the *coulomb*, i.e., an ampere second. The equivalent weight of silver (107.88 grams), then, or the equivalent weight of any other ion, would have associated with it $\frac{107.88}{0.001118}=96494$ coulombs. This number is called *the Faraday* (F †).

The *total electrical work* done by a cell, thus, if E is its voltage, is

$$96494 \times E \text{ volt-coulombs per equivalent,}$$

or

$$23074 \times E \text{ calories per equivalent.}$$

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* For problems illustrating the principles developed in this chapter, see Chapter X.

† Where we use the italic F to distinguish it from the Roman F, designating free energy.

Faraday's law is the basis of all our work in electrochemistry. This law may be expressed as follows:

1. *The weight of any one substance deposited by the electric current is proportional to the quantity of electricity passing through the electrolyte.*

2. *The weights of different substances deposited by the same quantity of electricity are proportional to their chemically equivalent weights.*

One gram-equivalent of H^+ ion (1 gram), as well as the gram-equivalent of any other ion, then will carry with it 96,494 coulombs; hence, 1 coulomb will cause 0.00001036 gram of hydrogen ion to separate as gas, or will cause the separation of $0.00001036 \times a$ grams of any other ion, where a is the equivalent weight of that ion.

The migration of the ions.—The chemical effect of the passage of an electric current through an electrolyte may be divided into two distinct portions, viz., the *conduction* through the electrolyte, and the *separation* of substance at the electrodes. It is not necessary that the ions which serve for the conduction of the current through the liquid be those which are also separated at the electrode, for *secondary reactions* (chemical reactions between the ions, or the decomposition of the substance separated) may take place there, causing others to appear as the result of the electrolysis. It is to be remembered, however, that even in such a case Faraday's law still holds, and the substances *separated* are always chemically equivalent in weight to those which would have been separated in case the secondary action had been avoided.

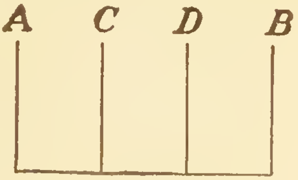
Although the two different effects are observed together in practice, we shall consider them separately; taking up the question of conduction here, and putting off that of separation to a later period.

The conduction through the liquid depends upon what we have designated thus far as ionized matter, and varies according to the *mobility* of this, which, in turn, is dependent upon the specific nature of the matter, its concentration, the temperature, and the nature of the solvent, as well as upon the viscosity of the solution.

After the electrolysis of a solution, *excluding, or allowing for, any secondary reaction,* it is found experimentally that the concentrations around the anode and cathode are not always identical, as they were initially. In some few cases they are, it is true, but in these it can be shown (as will be done later) that the mobility, i.e., velocity through the liquid at a certain voltage, is the *same* for the anion (negative ion), which goes to the anode, as it is for the cation (positive ion), which goes to the cathode. In all other cases the relative mobility, or relative speed of migration, through the liquid, is different for the two kinds of ionized matter of which the substance is composed. And, when the original solution is colored, this difference in concentration can be observed qualitatively by the eye.

And further than this, the analysis of the anode and cathode liquids after electrolysis, excluding secondary reactions, leads to an expression for the *relative mobilities*, i.e., *the transport* or *transference numbers* of the individual ions (n_A and n_C). The reasons for this change, together with the principle upon which its quantitative calculation is based, will be made clear by the following considerations:

Assume the vessel in the figure to be divided into three portions, *AC*, *CD*, and *DB*, and filled with a solution containing 30 gram equivalents of HCl. We have, then, 10 gram equivalents in each division. If 96,494 coulombs of electricity are passed through the cell from *A* to *B*, 1 gram equivalent of H^+ ion and 1 gram equivalent of Cl^- ion will be separated upon the electrodes *B* and *A*, if secondary action is excluded; *A* being the anode, to



which the chlorine goes, and *B* the cathode, to which the hydrogen goes. These gases we assume to be removed as they are formed. The 96,494 coulombs passing, as they do, through the whole solution, will have a certain effect upon the equilibrium of the ions. First we will imagine the H^+ and Cl^- ions to move with the same velocity, and then with differing velocities, and find the relation between the change in concentration and the relative mobilities in the two cases.

It is to be remembered here *that two oppositely electrified bodies composing a system will transport a current equal to the sum of the charges carried by the two bodies in the opposite direction,* for a negative charge going in one direction is equivalent to an equal and opposite charge going in the contrary direction. In other words, *all* of the current may be transported by the positive material, or a portion may be carried by each in opposite directions, and in all cases the total current is the *sum* of those currents going in the opposite directions. In this, electrolytic conduction differs from our general theories of the conduction of the current in a metallic wire.

I. If the velocity for the two ions is the same, then 1/2 gram equivalent of Cl^- ion, charged with 48,247 coulombs, will migrate from *BD* through *DC* to *CA*; and 1/2 gram equivalent of H^+ ion, with the same amount of electricity, will go from *AC* through *CD* to *DB*. Altogether, then, 1 gram equivalent, charged with 96,494 coulombs, has passed through the section *CD*. Since 1 gram equivalent of H^+ ion has been removed by decomposition from *BD*, i.e., from electrode *B*, and 1/2 gram equivalent has migrated to it, we have left $9\frac{1}{2}$ gram equivalents of H^+ ion and $9\frac{1}{2}$ gram equivalents of Cl^- ion, since but 1/2 gram equivalent of this has migrated from it. Consequently we have in *BD* $9\frac{1}{2}$ gram equivalents of HCl. In *AC* we have the same number, since 1 gram equivalent of Cl^- ion has disappeared from electrode *A* as gas, while 1/2 gram equivalent has migrated to it and 1/2 gram equivalent of H^+ ion has migrated from it. In the section *DC* the concentration is unaltered, i.e., just as much ionized matter has left it as has been carried to it.

The concentration at the anode (A) is the same as that at the cathode (B), then, after the electrolysis of a solution composed of ions with the same mobility, i.e., where $n_A = n_C$.

II. *Assume* the velocity of the H^+ ion to be five times that of Cl^-.

In this case, after 1 gram equivalent of H and 1 gram equivalent of Cl have separated as gases, the system will have undergone the following change. 5/6 of a gram equivalent of H^+ ion, charged with $\frac{5}{6}$(96,494) coulombs, will have migrated from *AC* through *DC* to *BD*, and 1/6 of a gram equivalent of Cl^- ion, with $\frac{1}{6}$(96,494) coulombs, will have gone from *BD* through *CD* to *AC*. And, as before, 1 gram equivalent of ion will have passed through the section *CD*, carrying with it 96,494 coulombs.

The original composition of the solution in *CD* is again unchanged. In *BD* we have lost 1 gram equivalent of H^+ ion in the form of gas, and gained 5/6 of a gram equivalent by the migration; consequently we have $9\frac{5}{6}$ gram equivalents of H^+ ion left. Since 1/6 of a gram equivalent of Cl^- ion has migrated from it, in *BD* we shall have $9\frac{5}{6}$ gram equivalents of HCl.

In *AC* we have lost 5/6 of a gram equivalent of H^+ ion, and 1 gram equivalent of Cl^- ion as gas, but have gained 1/6 of a gram equivalent of Cl^- by the migration; consequently we shall have $9\frac{1}{6}$ gram equivalents of HCl left.

From these two examples the following law may be deduced: *The loss on the cathode (B) is related to that on the anode (A) as the mobility of the anion* (n_A) *is to that of the cation* (n_C).

In this way Hittorf determined the *relative mobilities*, or *transport* or *transference numbers* of the various ions.

Determination of the migration ratios, or transport numbers.—The practical determination of the relative mobilities by this method is merely a matter of analysis. The apparatus which is used for this purpose is a decomposition-cell, so arranged that no metal can drop from one electrode to the other; or a U-tube may serve the purpose, so long as the two portions of liquid may be removed and analyzed separately. The apparatus is filled with solution and the current passed through for a certain length of time, the electrodes being of the metal which is contained in the salt, or of inert material, when certain possible secondary actions are to be avoided. After a certain time either the anode or cathode portion is withdrawn and analyzed. This analysis will give us the loss of metal on the one electrode, from which that on the other may be calculated; or, naturally, both sides may be analyzed.

If n_C is the fraction of the cation which has migrated from the anode to the cathode when one gram equivalent has been separated, then $1-n_C$ is that fraction of the anion which has gone to the anode. These two quantities, n_C and $1-n_C$ (or n_A), are called the *transport* or *transference numbers* of the cation and anion. We have then

$$\frac{n_C}{1-n_C}=\frac{\text{loss at anode}}{\text{loss at cathode}}.$$

An example of the calculation of the values of n_A and n_C is as follows: Hittorf electrolyzed a solution of $AgNO_3$ until 1.2591 grams of silver were separated. The volume of liquid at the cathode before the experiment gave 17.4624 grams of AgCl, and after it but 16.6796 grams, i.e., a loss of 0.7828 gram of AgCl or of 0.5893 gram of silver.

If no silver had come to the cathode by migration, the solution would have lost 1.2591 grams of silver; it lost, however, only 0.5893 gram; hence $1.2591-0.5893=0.6698$ gram silver has come to it by the migration. If just as much of the silver had come by migration as had been separated, the transport number of the Ag^+ ion would have been 1, i.e., the NO_3^- ion would not have migrated. Only 0.6698 gram of Ag^+ ion has migrated (loss at the anode), however; hence the transport number, the Ag^- ion in this concentration of $AgNO_3$ solution can be found by the proportion

$$1.2591 : 0.6698 :: 1 : n_C,$$

from which $n_C = 0.532$; and the transport number of the NO_2^- ion is

$$n_A = 1 - 0.532 = 0.468.^*$$

These values are not the same for all dilutions, although in general the variation is but slight.

A table containing a large number of results from experiments of this sort is given by Kohlrausch and Holborn, Leitvermögen der Elektrolyte, a few of which will be found in the table below:

HITTORF'S TRANSPORT NUMBERS FOR THE IONS

Substance. $\frac{N}{10}$	$1 - n_C$	Substance. $\frac{N}{10}$	$1 - n_C$
1/2 K_2SO_4	0.60	$LiCl$	0.70
1/2 $CuSO_4$	0.64	NH_4Cl	0.508
1/2 H_2SO_4	0.21	1/2 $BaCl_2$	0.61
1/2 K_2CO_3	0.37	1/2 $CaCl_2$	0.68
1/2 Na_2CO_3	0.48	1/2 $MgCl_2$	0.68
1/2 Li_2CO_3	0.59	HCl	0.21
KOH	0.74	KNO_3	0.50
$NaOH$	0.84	$NaNO_3$	0.61
KCl	0.507	1/2 $Ca(NO_3)_2$	0.61
$NaCl$	0.63	$KClO_3$	0.46

Naturally, inert anodes can also be used for this purpose; and in many cases, to avoid secondary reactions, an anode which is different from the metal of the salt *must* be used. Thus Hittorf (Ostwald's Klassiker der exakten Wissenschaften, Nos. 21 and 23) used cadmium as an anode in determining the transport numbers of the ions of sodium chloride, to avoid secondary and disturbing reactions.

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* Or, since the losses are known on the two sides, we have $\frac{n_C}{1 - n_C} = \frac{0.6698}{0.5893}$; from which the same values would be calculated.

This Hittorf method of determining the transport numbers, characterized as it is by the observation of the ratio of the amount of salt to a given amount of water at each electrode, is based upon the assumption that the solvent itself, water, for example, is not transported with the ionized materials. Another method, proposed by Nernst (Göttingen Nachricht., **56**, 86, 1900) modifies this, in so far that the reference substance in the analysis of the two solutions is not the solvent, *but another substance dissolved in the water* (*mannite, for example*), *which certainly is not transported by the current, either of itself, or as a compound or complex with the ions;* transport numbers determined in this way are known as "*true transport numbers.*"

The fact that the results by these two methods do not agree in all cases has been taken by various investigators * as showing qualitatively that the solvent, water, is in many cases actually transported in combination with the solute; and, finally, Washburn † was able to show that this is not only a fact, but to actually determine the amount of water transported with the equivalent weight of a number of ions, in terms of that transported by any one ion taken as a standard.

It is not only by such analytical methods as the above, however, that the transport numbers of the ions can be found, for it is possible to measure directly the actual speed of transport of a colored ion, in centimeters per second, by observing the speed of movement of the sharp color boundary existing between that solution and another, colorless, one, in a horizontal or vertical tube. From this the relative speeds, i.e., the transport numbers, of the two ions can be calculated; it would be necessary, however, in using this as a general method always to employ the same potential gradient, of 1 volt, for example.

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* Nernst-Gerrard-Offerman, l.c.; Morgan and Kanolt, Jour. Am. Chem. Soc., **28**, 572, 1906; and Buckböck, Zeit. f. phys. Chem., **55**, 563, 1906.

† Technology Quarterly, **21**, Nos. 31 and 37, 1908. Here is described a most accurate and satisfactory form of apparatus for the study of transport numbers, according to this method.

This method would not necessarily be restricted to colored ions, for the color boundary could be produced by a properly selected indicator; and as has been pointed out by Abegg and Steele the movement of the boundary can also be readily observed, even when the liquids are perfectly colorless, for the differing optical density is sufficient to distinguish the boundary of the two liquids sharply.

The final method for the determination of the transport numbers of ions, based upon this principle, was suggested by Denison and Steele (Zeit. f. phys. Chem., **57**, 110, 1906; Denison, Trans. Faraday Soc., **5**, 165, 1909; see also Lewis, Jour. Am. Chem. Soc., **32**, 862, 1910). The apparatus here consists of two electrode chambers, a straight tube and two small tubes into which the liquid can rise. To find the transport numbers of normal sodium chloride, for example, we would introduce the sodium chloride solution into the center tube, bounded on the one side by a solution (LiCl) in which the cation has a smaller mobility than the Na^+ ion, and on the other, sodium acetate, where the anion has a smaller mobility than the Cl^- ion. When a current is now passed through the apparatus, with electrodes of cadmium and lead peroxide, the two boundaries sharpen and move in opposite directions. Calling AA' the distance the sodium ion has been observed to move with the boundary between the solutions, naturally, with the positive current, and BB' the distance covered by the Cl^- ion, both for the same period of time, we have $n_C = \frac{AA'}{AA'+BB'}$, and $n_A = \frac{BB'}{AA'+BB'}$.

Lewis (l.c.) has shown that results such as are thus obtained, after certain corrections, are equal to the Hittorf values, and are not "true transport numbers"; but at the same time he shows how, by the addition to the system of a non-electrolyte which is not transported by the current, the "true transport numbers" can be calculated.

In certain cases, such as sodium chloride and potassium chloride, the numbers obtained by Denison and Steele with their method seemed at first to agree with the values of the "true transport numbers" as found by Washburn, using the method based upon analysis; but Lewis has pointed out that this was entirely accidental and due to the neglect of a correction which must always be made when the method of moving boundaries is employed.

When the substances separated at the electrodes are known, analysis of the liquids at the cathode and anode enables us to find the nature and composition of the ions into which the substances dissociates. In most cases, here, qualitative observations suffice for the purpose, and often changes in color make it possible to follow the process, even without analysis. Examples of the methods for the determination of ionic mobilities, in addition to those referred to above, will be found in the following papers: Noyes and Blanchard (J. Am. Chem. Soc., **22**, 729 and 732, 1900), Peters (Zeit. f. phys. Chem., **26**, 229, 1898), Calvert (ibid., **38**, 535, 1901), Morse (ibid., **41**, 709, 1902), McBain (Zeit. f. Elektrochem., **11**, 961), and for a review of all such work up to 1905, see McBain (Proc. Wash. Acad. Sci., **9**, 1, 1907).

B. The Conductivity of Electrolytes

Specific and equivalent conductivity.—*The specific conductivity* (κ) *of a solution is the reciprocal of its resistance in* *ohms when it is present between electrodes 1 square centimeter in area which are separated by 1 centimeter;* in other words, *the specific conductivity is the conductivity of a centimeter cube of the solution.* The specific conductivity, then, of a solution is a property which decreases in numerical value with decreased concentration, since the volume of the solution taken is always 1 cc., and its conductance is due almost exclusively to the amount of substance dissolved.

The equivalent conductivity, Λ, on the other hand, *is the conductivity, in reciprocal ohms, of that volume of the solution which contains 1 chemically equivalent weight of substance, the electrodes still being separated by 1 centimeter, and 1 centimeter wide, but high enough to contain between them the entire volume of solution.* The value of the *equivalent conductivity* can be found from the known specific conductivity of the solution, by aid of either of the following equations:

$$= \kappa \times 1000 \times v_e,^{*}$$

or

$$\Lambda = \frac{1000\kappa}{\text{equivalents per liter}}.$$

As will be seen the equivalent conductivity of a substance increases with decreased concentration, for while the same total amount of substance is always between the electrodes, the increased ionization with increased dilution causes it to conduct proportionally better. When the substance is completely ionized, i.e., when the specific conductivity would vary directly as the concentration, we see from the above equations that the equivalent conductivity would have attained a maximum and constant value. This value of the equivalent conductivity is called the *conductivity at infinite dilution*, and is

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[*] Where v_e is the volume of solution in liters containing the chemical equivalent weight in grams of the dissolved substance.

represented by Λ_∞, the equivalent conductivity at any other dilution of 1 equivalent in v_c liters being Λ_{v_c}.

Determination of electrical conductivity.—Since the degree of ionization of electrolytes can be determined most accurately by aid of the conductivity, the method is one of great importance. The apparatus used for this purpose was designed by Kohlrausch,* and is similar to that for determining the resistance of metals, except that an alternating current is used in place of the direct, and a telephone receiver instead of the galvanometer. The alternating current is used here to prevent actual decomposition of the solution, for that would decrease its concentration continually and cause polarization of the electrodes. With the alternating current, naturally, all substance which is deposited by the current in one direction is redissolved by it in the opposite direction, and all polarization effect is thus nullified.

The electrode vessel used for this purpose can be of any desired form so long as the electrodes are fixed rigidly in position, and can be thoroughly washed. The electrodes themselves are of platinum foil, and are coated electrolytically with platinum-black, so as to do away with any difference of potential which might exist between them, and thus give rise to a counter electromotive force.

It is not necessary in practice to have these electrodes just 1 square centimeter in cross-section or separated by 1 centimeter, for we can easily find the factor which will transform results for any cell into terms of specific conductivity. Kohlrausch has determined the specific conductivity of a number of standard solutions,† using a cell of exactly the specifications given in the definition.

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* For details see Ostwald, Handbook of Physicochemical Measurements, Macmillan Co. For an improved method for the determination of electrical conductivity with a degree of precision of from 0.01 to 0.001 per cent, see Washburn and Bell (Jour. Am. Chem. Soc., 35, 177, 1913).

† For a list of these values, see Landolt-Börnstein-Roth, Tabellen, 1912, page 1117.

A few of his values as observed for aqueous solutions of KCl at various temperatures are given in the table below:

AQUEOUS KCl SOLUTIONS [1]

$t°$.	Normal 74.59 gr. per liter		1/10 Normal.		1/50 Normal.		1/100 Normal.	
	κ	Λ_1	κ	Λ_{10}	κ	Λ_{50}	κ	Λ_{100}
0	0.06541	65.41	0.00715	71.5	0.001521	76.05	0.000776	77.6
10	0.08319	83.19	0.00933	93.3	0.001994	97.7	0.001020	102.0
20	0.10207	102.07	0.01167	116.7	0.002501	125.1	0.001278	127.8
25	0.11180	111.80	0.01288	128.8	0.002765	138.3	0.001413	141.3
30	....	....	0.01412	141.2	0.003036	151.8	0.001552	155.2
35	....	....	0.01539	153.9	0.003312	165.6		

Naturally, we can find from the above values the constant by which the conductivity as measured in reciprocal ohms in any one cell we are using, must be multiplied to give results for κ, i.e., based upon the centimeter cube. In such a case we would have simply the ratio:

$$\frac{\kappa}{\text{observed conductivity}} = \text{constant},$$

where κ is the specific conductivity taken from the table, and "observed conductivity" is the observed value in our cell for the same solution, at the same temperature. By multiplying our value for conductivity for any new liquid by this "constant" of the cell, we can thus obtain results directly in terms of specific conductivity. In this way we can use a cell of any constant size and yet obtain results in the units of the definition.

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[1] In these results for the dilute solutions, the specific conductivity of water is subtracted from the observed value. The Λ values are calculated from $\Lambda_{r_t} = \kappa \times 1000 \times v_t$.

Since the conductivity increases with the area of the electrodes, and decreases with increased separation, results obtained in a cell with electrodes of a known area, separated by a known distance, can also readily be calculated to area 1 and separation 1. The first method is very much more exact and satisfactory, however.

Ionic conductivities.—Since the ions (anion and cation) are the carriers of electricity in solution, the equivalent conductivity at any dilution divided by that at infinite dilution, i.e., when the substance is present only in the form of ions, will give us the degree of ionization. We have then

$$\alpha = \frac{\Lambda_{v_e}}{\Lambda_\infty}.$$

The maximum value for the equivalent conductivity at infinite dilution, Λ_∞, was found by Kohlrausch for a binary electrolyte *to be equal to the sum of two single values, one of which refers to the anion and the other to the cation. This law of the independent migration of the ions* shows that conductivity is an *additive property.* The truth of this law is shown by the table below, in the original Kohlrausch form:

EQUIVALENT CONDUCTIVITIES AT INFINITE DILUTION

	K	Na	Li	NH_4	H	Ag
Cl	123	103	95	122	353	...
NO_3	118	98	...	...	350	109
OH	228	201	...	...	...	...
ClO_3	151	...	...	...	...	103
$C_2H_3O_2$	94	73	...	...	...	83

Here we observe like differences between two corresponding sets of numbers in the vertical rows, and equal differences between any corresponding two in the horizontal ones, which can only occur when the result is composed of two single and independent values.

One kind of ion, then, always carries the same amount of electricity with its own velocity, independent of the nature of its companion ion. Although perhaps this table, which is only given for its historical interest, does not show conclusively that the conductivity is really an additive property, all later work has amply confirmed the law as rigid.

The equivalent conductivity at infinite dilution is consequently

$$\Lambda_\infty = \Lambda_C + \Lambda_A$$

where Λ_C and Λ_A are the equivalent conductivities due to the ions of the substance, when they are each present in the free state to the extent of 1 equivalent.

In a self-evident way, then,

$$n_C = \frac{\Lambda_C}{\Lambda_C + \Lambda_A} \quad \text{and} \quad n_A = 1 - n_C = \frac{\Lambda_A}{\Lambda_C + \Lambda_A},$$

in other words,

$$\Lambda_C = n_C \Lambda_\infty \quad \text{and} \quad \Lambda_A = n_A \Lambda_\infty,$$

where the terms n are the transport numbersof the ions (page 394) in that strength of that solution.

From the transport number of the ions of a salt, as found for a solution at infinite dilution, and its equivalent conductivity in the same state, *we can calculate, then, the equivalent conductivities of the anion and the cation.* In other words, by aid of Λ_∞, we can thus transform the ratios, the transport numbers, holding only for that specific solution, into values (Λ_C and Λ_A) which will hold in all solutions at any strength.

Thus the equivalent conductivity at infinite dilution Λ_∞

of sodium chloride is 110, while for the same condition $n_C=0.38$ and $1-n_A=0.62$, hence

$$\Lambda_C=0.38\times110=41.8(\mathrm{Na}^+),$$

$$\Lambda_A=0.62\times110=68.2(\mathrm{Cl}^-),$$

i.e., *1 equivalent of* Na^+ *ion possesses a conductivity of 41.8 reciprocal ohms when between electrodes 1 centimeter apart and large enough to contain between them the total volume of solution in which the sodium ion exists; and 1 mole of* Cl^- *ion under the same conditions has a conductivity equal to 68.2 reciprocal ohms.*

In all solutions in the same solvent, at the same temperature, these values (Λ_C or Λ_A) remain constant, so that it is possible for us to calculate what the conductivity for any substance composed of them would be at infinite dilution. This is of great value in experimental work, for it is not always possible to actually reach this limiting value, with any great degree of accuracy, for the solution of that substance itself.

A table of such results, then, enables us to find the limiting value of the conductivity at infinite dilution, and not only this, for

$$\Lambda_v=\alpha(\Lambda_A+\Lambda_C),$$

i.e., *if we know the fraction of a mole of each ion present we can find the equivalent conductivity of the solution at any dilution by multiplying the sum of the ionic conductivities by the degree of ionization.*

Since most neutral salts are very largely ionized the value of the equivalent conductivity at infinite dilution can be readily determined in very many cases. By subtracting the value for the metal ion from this result it is possible, then, to find the ionic conductivity of the acid radical which is present as the negative ion. In the table below are given a few ionic conductivities, found in this way, from which various values may be calculated:

IONIC CONDUCTIVITIES AT 18° [1]

	Λ.	Temp. Coeff. β.		Λ.	Temp. Coeff. β.
Li^+	33.44	0.0265	$\frac{1}{2}Zn^{++}$	45.6	0.0251
Na^+	43.55	0.0244	$\frac{1}{2}Mg^{++}$	46.0	0.0256
K^+	64.67	0.0217	$\frac{1}{2}Ba^{++}$	56.3	0.0238
Rb^+	67.6	0.0214	$\frac{1}{2}Pb^{++}$	61.5	0.0243
Cs^+	68.2	0.0212	$\frac{1}{2}SO_4^=$	68.7	0.0227
NH_4^+	64.4	0.0222	$\frac{1}{2}CO_3^=$	70	0.0270
Tl^+	66	0.0215	BrO_3^-	46.2	......
Ag^+	54.02	0.0229	ClO_4^-	64.7	......
F^-	46.64	0.0238	IO_4^-	47.7	......
Cl^-	65.44	0.0216	MnO_4^-	53.4	......
Br^-	67.63	0.0215	CHO_2^-	46.7	......
I^-	66.40	0.0213	$C_2H_3O_2^-$	35	......
SCN^-	56.63	0.0211	$C_3H_5O^-$	31	......
ClO_3^-	55.03	0.0215	$C_4H_7O_2^-$	27.6	......
IO_3^-	33.87	0.0234	$C_5H_9O_2^-$	25.7	......
NO_3^-	61.78	0.0205	$C_6H_{11}O_2^-$	24.3	......
H^+	318	......	$\frac{1}{2}C_2O_4^=$	62.7	......
OH^-	174	......	Picrate ion	26	0.0258

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[1] See Kohlrausch, Berl. Akademieber., 26, 581, 1902, and Sitzungsber. d. Akad. d. Wiss. zu Berlin, 26, 572, 1902; Bredig, Z. f. phys. Chem., 13, 191, 1894; and Gorke, *ibid.*, 61, 495, 1908.

The temperature coefficients here are the percentage change in ionic conductivity per centigrade degree; i.e., are the values of β in the equation

$$\Lambda_{C,t} = \Lambda_{C,18}[1+\beta(t-18)],$$

i.e.,

$$\beta = \frac{\Lambda_t - \Lambda_{18}}{\Lambda_{18}(t-18)}.$$

This same type of equation holds also for the conductivity of the ordinary solution of a substance composed of two ions, i.e., for $\Lambda_{v_e \cdot t}$.

While the equivalent conductivity of a substance increases with the temperature, owing to decreased friction, etc., the corresponding change is not noticed in the value of the degree of ionization, α, for it must be remembered that Λ_∞ will also increase with the temperature. As a matter of fact, notwithstanding the increased value of the conductivity at high temperatures, we find that in all cases of dissolved substance the *degree of ionization decreases with increased temperature.*

The ionic conductivity of elementary ions is a periodic function of the atomic weight and rises with it in each series of analogous elements; but analogous elements with atomic weights greater than 35 have approximately equal conductivities.

Isomeric and metameric anions have the same equivalent conductivities.

In finding the values of Λ_v for solutions, it is necessary to take into account the viscosity of the solution, for upon the internal friction, naturally, would depend the speed of migration of the ions and also consequently the amount of current conducted. The usual form of application of this correction is given by the equation

$$\alpha = \frac{\Lambda_{v_e}}{\Lambda_\infty}\left(\frac{\eta_{v_e}}{\eta_\infty}\right),$$

where $\left(\frac{\eta_{v_e}}{\eta_\infty}\right)$, (a term giving the ratio of the viscosities of the two solutions, at v_e liters and at ∞ liters) becomes unity for sufficiently dilute solutions. The importance of this correction is shown by the fact observed by Kraus and Bray (l.c.) that it amounts to 1.8% for a twice normal aqueous solution of KCl. It has been shown by Walden (Zeit. f. phys. chem., 55, 207, 1906) in this connection, that for a large number of *organic solvents* the temperature coefficients at infinite dilution of viscosity and conductivity are identical; and Noyes has shown a similar relationship for certain aqueous solutions.

In the calculation of α, as will be seen, the value of Λ_∞ must be found with perhaps greater precision than that attained in the Λ_C and Λ_A values above. It can be shown in this connection that an error of but 0.1% in Λ_∞ at 18°, produces an error of 1.7% in the value calculated for the un-ionized portion of a 0.01 normal solution, and an error of over 4.7% at 0.001 normal. For a review of the various methods that have been suggested for the accurate estimation of the value of Λ_∞, see Bates (Jour. Am. Chem. Soc., 35, 519–535, 1913), and also Kendall (Trans. Chem. Soc., 101, 1275–1296, 1912).

The absolute mobility of the ions.—We found above that the actual speed of transport of an ion could be measured in centimeters per second by observations of the movement of a boundary surface between liquids. Let us now consider how such a value could also be calculated from what we now know of the behavior of a substance when an electric current is passed through its solution.

Imagine two electrodes 1 centimeter apart, and assume that between them we have 1 equivalent of positive ion with 1 equivalent of negative ion. Then in one second the amount of electricity Λ_∞ will go through the liquid. As each equivalent of ion could transport 96,494 coulombs, the ratio $\frac{\Lambda_\infty}{96494}$ must give the fraction of the 1 centimeter which the ions together have traversed in one second, i.e., the sum of their velocities in centimeter-seconds. In other words the distance traversed by the cation will be $\frac{\Lambda_C}{96494}(=U_C)$ and that by the anion $\frac{\Lambda_A}{96494}(=U_A)$ both in centimeter-seconds; for $\Lambda_\infty=\Lambda_C+\Lambda_A$ and consequently $\frac{\Lambda_\infty}{96494}=\frac{\Lambda_C}{96494}+\frac{\Lambda_A}{96494}$.

The equivalent conductivity of a 0.0001 normal solution of KCl at 18° (in reciprocal ohms) is 128.9; the sum of the distances traversed by the two ions, then, is

$$\frac{128.9}{96494}=0.001336 \text{ cm. per second.}$$

This total velocity is made up of the two single velocities. From Hittorf's experiments we find that the relative velocities of K^+ and Cl^- ions in KCl, i.e., n_C and n_A, are as 49 is to 51. Hence, at 18°, K^+ has a velocity of 0.00066 cm. per second, and Cl^- has a velocity of 0.00069 cm. per second for a potential gradient of 1 volt.

In the table below are some of the absolute mobilities as calculated by Kohlrausch:

ABSOLUTE VELOCITY OF THE IONS AT 18° IN CMS. PER SECOND

$K^+ = 0.00066$
$NH_4^+ = 0.00066$
$Na^+ = 0.00045$
$Li^+ = 0.00036$
$Ag^+ = 0.00057$
$Cr_2O^{7=} = 0.000473$

$H^+ = 0.00320$
$Cl^- = 0.00069$
$NO_3^- = 0.00064$
$ClO_3^- = 0.00057$
$OH^- = 0.00181$
$Cu^{++} = 0.00031$

It has been possible to prove the correctness of some of these results by experiment, i.e., by actual speed measurements of a color boundary in a tube, see Whetham (Phil. Trans., 1893A, 337; 1895A, 507).

In the table below the calculated and observed values for Cu^{++}, Cl^- and $Cr_2O_7^=$ are compared:

COMPARISON OF ABSOLUTE IONIC VELOCITIES

Ion.	Whetham, by Experiment.	Kohlrausch, Calculated.
Cu^{++}	0.00026 0.000309	0.00031
Cl^-.............	0.00057 0.00059	0.00069
$Cr_2O_7^=$.........	0.00047 0.00048 0.00046	0.000473

The basicity of an acid.—As we have seen, weak polybasic acids ionize in general up to a value of $\alpha = 0.5$ as if they were monobasic. And in all such cases it would require a dilution of one equivalent in many million liters to arrive at complete ionization, i.e., to remove all replaceable hydrogen from the negative ion. In the case of the neutral salts of these acids, on the other hand, the dissociation into more than two ions takes place at a much smaller dilution. The difference of conductivity, then, between two dilutions must be greater for the neutral salt of a polybasic acid than for one of a monobasic one. Ostwald has made use of this fact for the determination of the basicity. He found empirically that the *sodium salt* of a monobasic acid gives a difference in equivalent conductivity at $v_e=32$ liters and $v_e=1024$ liters of approximately 10 units, a dibasic one of 20 units, etc. Hence to find the basicity of an acid we have only to find the equivalent conductivity of its Na salt at 32 and 1024 liters dilution; then n, the basicity of the acid, is given by $n=\frac{\Delta}{10}$.

VALUES OF Δ AND n FOR SODIUM SALTS OF ORGANIC ACIDS

Acid.	Δ	$n=\frac{\Delta}{10}$
Formic	10.3	1
Acetic	9.5	1
Propionic	10.2	1
Benzoic	8.3	1
Quininic	19.8	2
Pyridin-tricarboxylic (1, 2, 3)	31.0	3
" (1, 2, 4)	29.4	3
Pyridin-tetracarboxylic	41.8	4
Pyridin-pentacarboxylic	50.1	5

The conductivity of neutral salts.—Another empirical law enables us to find the equivalent conductivity of a neutral salt at one dilution, if we know it for another, and provided the salt is largely ionized, i.e., when Λ_{v_e} is not very different from Λ_∞. The relation observed is as follows:

$$\Lambda_\infty - \Lambda_{v_e} = n_1 \cdot n_2 \cdot c_v,$$

or

$$\Lambda_\infty = n_1 \cdot n_2 \cdot c_v + \Lambda_{v_e},$$

where n_1 and n_2 are the valences (i.e., number of equivalents in an ion) of the anion and cation respectively, and c_v is a constant for all electrolytes. When c_v is known for all dilutions, and also the terms Λ_{v_e}, n_1, and n_2, we can find the value of Λ_∞, i.e., the equivalent conductivity at infinite dilution. If we designate $(n_1 \cdot n_2 \cdot c_v)$ by d_v, then

$$\Lambda_\infty = \Lambda_v + d_v.$$

The table below gives the value of d_v at different dilutions for values of $n_1 \cdot n_2$ equal to 1, 2, and 4 at both 18° and 25°.

VALUE OF d_v IN ABOVE EQUATION

v_e	Equiv. per liter.	Both ions univalent.		1 ion uni- and the other bi-valent.		Both ions bi-valent.	
		18°	25°	18°	25°	18°	25°
10000	0.0001	1.0	1.1	2.0	2.3	5	6
5000	0.0002	1.4	1.6	2.8	3.2	7	8
2000	0.0005	2.0	2.3	4.4	5.1	11	13
1000	0.001	2.7	3.1	6.1	7.0	16	18
500	0.002	3.6	4.2	8.3	9.6	23	26
200	0.005	5.5	6.3	12.3	14.2	33	38
100	0.01	7.5	8.6	16.5	19.0	42	48
50	0.02	9.8	11.3	21.5	24.5	51	58

This behavior may be summed up in words as follows: *The change in equivalent conductivity with the dilution is roughly constant for salts of the same type; and the change in equivalent con-*

ductivity for salts of different types is proportional to the valences of the constituent ions.

This is similar, as will be noted, to the relations already considered between the ionization of salts of the same or differing type (pp. 214–217); in fact, they were derived from this.

The ionization of water.—The ions of water are H^+ and OH^-, i.e., to a very slight degree it is a binary electrolyte. The specific conductivity κ of a specially purified water was found by Kohlrausch to be

$0.014 \cdot 10^{-6}$ at 0° C.
$0.040 \cdot 10^{-6}$ at 18°
$0.055 \cdot 10^{-6}$ at 25°
$0.084 \cdot 10^{-6}$ at 34° C.
$0.17 \cdot 10^{-6}$ at 50°

From this conductivity the degree of ionization is easily determined. One mole of H^+ ion has a conductivity equal to 318 units (p. 405), while 1 mole of OH^- ion has one equal to 174; hence the maximum molecular conductivity of water should be $\Lambda_\infty = 318 + 174 = 492$, if completely dissociated. The conductivity of a liter of water, from the above data, between electrodes 1 centimeter wide and separated by 1 centimeter, and high enough to contain between them 1000 cc. at 18° will be 10^3 times as large as 0.04×10^{-6}, i.e.,

$$0.04 \times 10^{-6} \times 10^3 = 0.04 \times 10^{-3}.$$

Since if this liter contained 1 equivalent of H^+ ion and 1 equivalent of OH^+ ion its equivalent conductivity would be 492; we have, then,

1 eq. of H^+ per liter : 492 :: x eq. of H^+ (or OH^-) per liter : 0.04×10^{-3},

i.e.,

$x = c_{H^+} = c_{OH^-} = \dfrac{0.04 \times 10^{-3}}{492} = 0.8 \times 10^{-7}$ equivalents (moles) per liter, which is the concentration of H^+ and OH^- ions at 18°, i.e., there are 17 grams of OH^- and 1 gram of H^+ ion in 12,000,000 liters of water.

It is to be remembered here that the 492 would be the value if 1 mole of H^+ ion and 1 mole of OH^- ion were present together between electrodes 1 cm. apart and of any cross-section, so long as they would contain between them the amount of liquid. Since we use water as a solvent, however, the equivalent conductivity of water itself is usually calculated for a liter, and not, as it might be assumed by definition, 18 grams. The calculation was similar in determining the ionic product of H^+ and OH^- ions (p. 347), where s_{H_2O} was equal to $\frac{1000}{18}K$, i.e., $55.5K$.

Determination of hydrolytic dissociation from the conductivity.—When a salt reacts with 1 mole of water, and either the base, the acid or both, are appreciably ionized, the larger the hydrolytic dissociation, the greater will be the equivalent conductivity, up to $\Lambda_{acid}+\Lambda_{base}$ as a limit. The increase of conductivity for the dissociation α will be $\Lambda_2-\Lambda_1$, when Λ_2 is the actual equivalent conductivity of the water solution of the salt, and Λ_1 is the equivalent conductivity without hydrolytic dissociation at the same concentration. (This is found from the conductivity of the salt in the presence of an excess of one of the products, subtracting from it the conductivity of the added substance, if it has any.) $\Lambda_{acid}+\Lambda_{base}-\Lambda_1$ is the increase of conductivity, then, that would be observed if the hydrolysis were complete. Hence

$$\alpha=\frac{\Lambda_2-\Lambda_1}{\Lambda_{acid}+\Lambda_{base}-\Lambda_1},$$

where $\Lambda_{acid}+\Lambda_{base}$ is the sum of the conductivities of the acid and base *at the same dilution as the salt.*

An example of the calculations in this way is the following:

At 25°, $v_c=197.6$. $\Lambda_{126.7}$ for aniline hydrochloride is 126.7;

Λ for aniline hydrochloride plus an excess of aniline is 106.6; Λ_{HCl} is 415 ($v_e = 197.6$). The conductivity of aniline is negligible. Find the degree of hydrolytic dissociation.

Here $126.7 - 106.6$ is the actual increase in conductivity due to the hydrolytic dissociation α. If the hydrolysis were complete this increase would be $415 - 106.6$; hence

$$\alpha = \frac{126.7 - 106.6}{415 - 106.6} = 0.0652.$$

It is conceivable here that instead of an increase in conductivity due to the hydrolysis a decrease might occur, i.e., where the acid, at the dilution of the salt, has a smaller conductivity than the salt. Then it would be necessary simply to change the ratio so as to give the actual decrease to the decrease caused by $\alpha = 1$.

For the method to be used in case both acid and base are very slightly ionized, see Lundén, J. chim. Phys., 5, 145 and 574, 1907, and Noyes, Carnegie Publication No. 63.

The conductivity of difficultly soluble salts.—If the saturated solution of any insoluble salt is so dilute that we may assume complete dissociation, $\Lambda_\infty = \Lambda_{v_e}$, we have

$$\kappa_{\text{solution}} - \kappa_{H_2O} = \kappa,$$

and

$$\Lambda_{v_e} = \Lambda_\infty = \kappa \times 1000 v_e,$$

i.e.,

$$v_e = \frac{\Lambda_\infty}{\kappa \times 10^3}$$

and

$$c = \frac{1}{v_e} = \frac{\kappa \times 10^3}{\Lambda_\infty} \text{ equivalents per liter.}$$

This method has been used by Holleman* and Kohlrausch and Rose † with very good results. In this way a number of solubilities have been determined; although it is usually customary for more accurate work, to first find the approximate dilution in this way, and then by aid of the table on page 410 to find from it and Λ_{v_e} a more accurate value to be used in place of Λ_∞, the final value of $v_e = \frac{1}{c}$ being calculated from that.

The salts employed here are of course so insoluble that it is impossible to find the term Λ_∞ by direct experiment. Its value, however, can be found from the general equation

$$\Lambda_\infty(MX) = \Lambda_\infty(MX_1) + \Lambda_\infty(M_1X) - \Lambda_\infty(M_1X_1),$$

where M and M_1 represent metals and X and X_1 the negative radicals.

Thus from

$$\left.\begin{array}{ll} \Lambda_\infty, \text{ for } \frac{1}{2}BaCl_2, & = 115 \\ \Lambda_\infty, \text{ for } KCl, & = 122 \\ \Lambda_\infty, \text{ for } \frac{1}{2}K_2SO_4, & = 128 \end{array}\right\} 18^\circ$$

we have, subtracting the second from the sum of the first and third

$$\Lambda_\infty, \text{ for } \frac{1}{2}BaSO_4, = 115 + 128 - 122 = 121.$$

This value could also be found from the table illustrating Kohlrausch's law of the independent migration of the ions, of which it is an application, or from that on p. 405. Naturally, solubilities calculated from this value of Λ_∞ would be expressed in liters containing 1 *equivalent*, while solubilities are usually expressed in moles per liter. The v_e directly found for $\frac{1}{2}BaSO_4$, then, must be multiplied by two to give the volume containing 1 *mole;* and the solubility in moles per liter would be $c=\frac{1}{2v_e}$. It must be borne in mind here that this method is only applicable, in its simpler form, when we can safely assume Λ_{v_c} for a saturated solution to be the same as Λ_∞. And further, it is limited to those substances which are soluble enough to give a value of κ which differs appreciably from that for the water used. A silver iodide solution in this respect seems to be about on or just beyond this limit.

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* Zeit. f. phys. Chem., 12, 125, 1803.

† *Ibid.*, 234, 1893.

The dielectric constant and dissociating power. Other solvents than water.—According to J. J. Thomsen and Nernst, there is a relationship between the dielectric constant of the solvent, and its power of ionizing dissolved substances. The dielectric constant is determined by placing the substance between two plates between which there is a certain potential difference, and measuring the loss of potential. Air is used first between the plates, and then the substance to be determined. The factor which we measure is the specific inductive capacity of the liquid for electricity, referred to air as a standard. For the observed values of the dielectric constant for various liquids and other substances see Landolt-Börnstein-Roth, Tabellen, 1912, 1212–1223.

As the constant for water (80.0) is very much higher than for any of the other solvents, its dissociating power should also be the greatest.

The recent work of Kraus and Bray (l.c., 1217) in developing their empirical dilution law has had much to do with removing the discrepancies apparently existing between the Nernst-Thomsen rule and experimental fact. These authors compare not the ionization of the salt, but the values of the constants of their general equation

$$\frac{(c\alpha)^2}{c(1-\alpha)}=K+D(c\alpha)^m,$$

with the dielectric constant of the solvent. They find in this way that the value of constant D is practically independent of the nature of the solvent, so long as its dielectric constant is less than 22. In fact it is certain that as the dielectric constant approaches unity, the value of D does not approach zero—which means that the power to ionize is not restricted to solvents of high dielectric constants. Only in relatively dilute solutions, where the K-term predominates, is the ionizing power confined to solvents with high dielectric constants. The value of K decreases very rapidly with a decreasing value of the dielectric constant. Thus for water, dielectric constant $=80$, K has approximately the value 0.1, while for methylamine, whose dielectric constant is 10, the value of K is roughly 0.0001. With decreasing dielectric constant, K increases the more rapidly, the higher the constant; and is roughly proportional to the cube of the dielectric constant. As the dielectric constant approaches unity, K becomes vanishingly small.

With respect to its effect upon the value of m, it is observed that as the dielectric constant approaches unity, m increases to a value equal to 2.

The discrepancies of the Nernst-Thomsen rule hitherto observed when it was applied to the values of α, thus disappear completely, when the comparison is made for a given solute in various solvents between the dielectric constant and the constants of the Kraus and Bray empirical dilution law.

C. Electromotive Force

Determination of the electromotive force.—In all the cases we are to consider in this section, it is necessary that the electromotive force be measured by aid of the compensation method, i.e., that as little actual current be taken from the cell as is possible, otherwise the cells employed will become polarized.

As the basis of such methods is a known and constant electromotive force, the standard cell is an exceedingly important part of the measurement. The standard cells in general use in this work are of two kinds, one of which has a fixed constant value, while the other may be made up in such a way as to give one of several values.

Of the former type is the well-known Clark cell, which consists of amalgamated Zn in a paste of $ZnSO_4$, as one electrode, and Hg in a paste of Hg_2SO_4 as the other. This cell gives and E.M.F. equal to

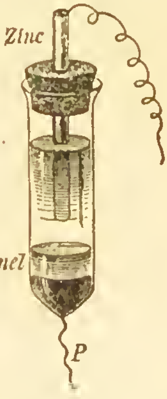
$$E_t = 1.4325 - 1.19 \times 10^{-3}(t - 15°) - 0.7 \times 10^{-5}(t - 15°)^2 \text{ volts.}$$

Another standard cell of the same type which is in common use is the cadmium element (Weston). This is made up with electrodes of mercury and cadmium amalgam according to the following scheme, the Hg being the positive pole, the Cd the negative:

Hg in a paste of $Hg_2SO_4 + CdSO_4$
sat. $CdSO_4$ solution + crystals
paste of $CdSO_4$ – Cd amalgam.

The electromotive force of this cell, by international agreement, is taken as

$$E_t = 1.0183 - 3.8 \times 10^{-5}(t - 20°) - 0.65 \times 10^{-6}(t - 20°)^2 \text{ volts.}$$



The Helmholtz element, a cell of the second type, see figure, consists of amalgamated Zn in $ZnCl_2$ solution (sp. gr. = 1.409 at 15°), calomel, and Hg. This gives an E.M.F. approximately equal to 1 volt, but its exact value depends upon the specific gravity of the $ZnCl_2$ solution, so that it must always be standardized by comparison with a Weston or Clark element. Its great advantage is its very small temperature coefficient, which at low temperatures is negligible.*

Types of cells.—Cells are either reversible or non-reversible, according as the process may be reversed or not. A reversible cell can always be put in its original condition again by sending a current through it in the opposite direction, while with a non-reversible cell this is not possible. A typical reversible cell is the Daniell, where we have metallic Cu in a $CuSO_4$ solution, and metallic Zn in $ZnSO_4$ solution. The zinc dissolves in this cell and the copper is precipitated upon the electrode during the action, but by passing a current through it from Cu to Zn, the Zn is precipitated, while Cu is dissolved, until the original state is again reached.

An example of a non-reversible cell, on the other hand, is one from which a gas is given off, for the passage of the current cannot cause the gas to recombine. Here we shall consider principally the reversible type.

The chemical or thermodynamical theory of the cell.—The simplest theory of the action of a reversible cell was advanced by Helmholtz and Thomson. According to this, the chemical energy of the process is transformed completely into electrical energy. This theory in the form in which it was advanced, however, has proven to be incorrect, for it holds only for the Daniell cell. The explanation of the variation in the case of other cells was offered by Gibbs and Helmholtz independently, who proved it to be due to a temperature-coefficient.

Assume a reversible primary cell in which the amount of heat Q is liberated or absorbed per equivalent. Imagine this cell in a temperature-bath so that the cell remains at constant temperature,—i.e., if heat is absorbed it is replaced, or if heat is liberated it is removed—thus preventing the heat,

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* For further details of these measurements, cells, etc., see Ostwald's Physico-chemical Measurements, Macmillan.

Q, involved in the reaction from causing a change in the temperature in the cell.

It is quite evident, here, if the chemical energy (as heat) of a reaction is being transformed completely into electrical energy, and no heat is either evolved or absorbed as the reaction progresses, that the chemical energy transformed is equivalent to the electrical energy produced, i.e.,

$$\text{chemical energy} = \text{electrical energy},$$

if both forms of energy are expressed in like units.

If the reaction evolves or absorbs heat, however, it will be necessary, to retain the temperature constant, to remove or supply heat to the system, and it is clear that this will involve either a decrease or increase in the electrical energy produced. In short, in addition to the chemical energy, we must know the effect of this absorbed or liberated heat upon the electrical energy, if the total amount produced by the cell is thus to be calculated. This can be found by aid of the following ideal cyclic process: Heat the cell from the temperature T to $T+\Delta T$. The electromotive force will then go from E to $E+\Delta E$. The cell is now allowed to run until the amount of current F has been developed. In order that the cell may be retained at this constant temperature, the heat $Q+\Delta Q$ must be absorbed, and the electrical work done by the cell will be $F(E+\Delta E)$.

Next cool the cell again to T, where the electromotive force is E, and send the amount of current F through it in the opposite direction, thus doing the electrical work FE. Heat equal to Q must be removed to keep the temperature constant at this point, and, provided the cell is reversible, all will again attain its original condition.

The total work involved in the above cycle of operations is $F(E+\Delta E)-FE$, i.e., $F\Delta E$, and the amount of heat ΔQ has been transformed into work, hence by the 2d law of thermodynamics (p. 66) we have

$$\frac{\Delta Q}{Q}=\frac{F\Delta E}{Q}=\frac{\Delta T}{T},$$

i.e.,

$$Q=FT\frac{\Delta E}{\Delta T},$$

and the correct general relation between the chemical and electrical energies becomes

$$\text{electrical energy}=FE=\text{chemical energy}+FT\frac{dE}{dT},$$

or

$$E=\frac{\text{chem. energ.}}{F}+T\frac{dE}{dT}.$$

The electrical energy producible from the chemical energy developed by a reaction is equal to the heat of the chemical reaction, expressed in electrical units, plus the absolute temperature times the temperature coefficient of the electrical energy; which may be either positive or negative.*

The actual electromotive force, E, is only equal to that calculated directly from the chemical energy when $\frac{\Delta E}{\Delta T}=0$, for then the electromotive force does not change with the temperature. Otherwise E is smaller or greater than $\frac{\text{chem. energ.}}{F}$, according as $T\frac{dE}{dT}$ is negative or positive.

The Daniell cell has such a small temperature coefficient that the electrical energy is nearly equal to the chemical energy. For other cells, it is possible to determine the temperature coefficient, and thus from the chemical energy to calculate the electromotive force of the cell. The results by experiment and calculation agree in most cases within the experimental error, showing that this conception of the process is correct. We see, then, that the amount of heat generated by the chemical process is no criterion of the amount of electrical energy involved, for heat which is absorbed from the environment may also be transformed into electrical energy, while in other cases less heat may be transformed into electricity than is given up by the chemical process.

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* See page 389.

An example of the application of this formula is given by the Grove gas cell. Here

$$E = 1.062 \quad \text{and} \quad Q = 34200 \text{ cals.},$$

hence

$$1.062 = \frac{34200}{23074} + T\frac{dE}{dT}, \quad \text{i.e.,} \quad T\frac{dE}{dT} = -0.42 \text{ volt},$$

in place of -0.416 as found by experiment.

Electromotive force and the criterion of equilibrium.—From what was said on page 257, it will be seen that the concept of the change in the free energy of a chemical reaction can be used to correlate the electrical (maximum) work performable by the reaction, with its criterion of equilibrium. It is evident, in such a case, that we would have

$$-\Delta \mathrm{F} = n_e F E \text{ volt-coulombs or joules,*}$$

where n_e is the number of chemical equivalents involved in the reaction. For a typical chemical reaction, such as that on page 251, however, we know also that

$$-\Delta \mathrm{F} = RT \log_e K_p - RT \log_e \frac{p_0^{N_1'} p_0^{N_1'}}{p_0^{N_1} p_0^{N_2}},$$

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* One joule is equal to 10^7 ergs, while 1 calorie is equal to 4.182×10^7 ergs. Since the electrical work of the cell (page 389) is equal to 96,494 E joules, then, it must therefore be equal to 23,074 E calories, *per equivalent*.

where the second term involves the pressure of the original substances before reaction, and those of the products formed by the reaction; and becomes 0 ($\log_e 1$) when these are equal to the unit pressure of 1 atmosphere.

By substituting for $-\Delta F$ in this equation the value given in the previous one, we obtain, as the relationship existing between the electrical work available, and the terms determinable from the equilibrium and initial states of the chemical reaction,

$$n_e FE = RT \log_e K_p - RT \log_e \frac{p_0{}^{N_1'} p_0{}^{N_2'}}{p_0{}^{N_1} p_0{}^{N_2}},$$

or

$$E = \frac{2T}{23074 n_e}\left(\log_e K_p - \log_e \frac{p_0{}^{N_1'} p_0{}^{N_2'}}{p_0{}^{N_1} p_0{}^{N_2}}\right) \text{ volts.}$$

Let us apply this equation to illustrate its use, to the hydrogen-oxygen gas cell, and calculate its electromotive force at 17° C. This cell is made up of platinum electrodes in, for example, an aqueous solution of sulphuric acid, one electrode being exposed to gaseous hydrogen and the other to oxygen; the electrodes in each case standing half in the solution and half in the gas. The chemical reaction taking place in the cell is

$$2H_2 + O_2 \rightleftarrows 2H_2O,$$

where 4 equivalents of hydrogen, with 4 equivalents of oxygen are transformed into 2 moles of water, i.e., $n_e = 4$.

According to the law of mass action, we have as the criterion of equilibrium of this reaction,

$$K_p = \frac{p^2_{H_2O}}{p^2_{H_2} p_{O_2}};$$

so that if p'_{H_2} and p'_{O_2} are the original pressures of the two gases respectively before the reaction, and p'_{H_2O} is the pressure of the water vapor produced by the reaction (which is, naturally, constant at any one temperature, and hence equal to the value p_{H_2O}) we have for the electromotive force produced by the chemical system when arranged as a cell, at 17° C.,

$$E=\frac{2\times 290}{4\times 23074}\left(\log_e \frac{p^2_{H_2O}}{p^2_{H_2}p_{O_2}}-\log_e \frac{p'^2_{H_2O}}{p'^2_{H_2}p'_{O_2}}\right) \text{ volts,}$$

which reduces, since $p_{H_2O}=p'_{H_2O}$, for the original pressure values of hydrogen and oxygen values of $p'_{H_2}=1$; $p'_{O_2}=1$ atmosphere, to

$$E=\frac{2\times 290}{4\times 23074}\left(\log_e \frac{1}{p^2_{H_2}p_{O_2}}\right) \text{ volts.}$$

The pressures of hydrogen and oxygen gases existing in equilibrium with water vapor at 17° (which has a pressure equal to 0.0191 atmosphere) are $p_H=0.0191\times 1.8\times 10^{-27}$ and $p_{O_2}=\frac{1}{2}(0.0191\times 1.8\times 10^{-27})$. Substituting these values in our final equation, and transforming the logarithms to the base *e*, to those to the base 10, we find

$$E=\frac{2\times 290}{4\times 23074}(\log_e 4.92\times 10^{85}=0.01447 \log_{10} 4.92\times 10^{85}=1.24$$

volts, as the electromotive force of a cell producing water vapor from gaseous oxygen and gaseous hydrogen, both at a pressure of 1 atmosphere.

Perhaps it is better here, in general, to write the free energy equation in two parts, one referring to the maximum work of the process at each electrode, for in that way less confusion can arise as to the value of n_e in any definite case. See Lewis (Jour. Am. Chem. Soc., **35**, 23, 1913).

For other examples of the application of the concept of free energy to the calculation of electromotive force, see Preuner (Zeit. f. phys. Chem., **42**, 57, 1903), Nernst and von Wartenberg (*ibid.*, 56, 534, 1906), Haber (Thermodynamics of technical gas reactions (Lamb) pages 324-332) and Tolman and Ferguson (Jour. Am. Chem. Soc., 34, 232–246, 1912).

The osmotic theory of a cell.—Considering a cell from the standpoint of our conclusions respecting the nature of electrolytes in solution, it is possible to see more clearly into the cause of the rise of a difference of potential between two solutions, or between a metal and a solution.

Assume that we have two solutions in contact, and that they contain the same *monovalent* ions in different concentrations. The difference of potential existing on their boundary can be calculated by aid of the following process of reasoning: If Λ_A and Λ_C are the mobilities of the respective ions, then, by the passage of 96,494 coulombs of electricity, the following changes take place: If the current enters on the concentrated side and passes through both solutions, $\frac{\Lambda_C}{\Lambda_C+\Lambda_A}$ gram equivalents of positive ion will go from the concentrated to the dilute solution, and during the same time $\frac{\Lambda_A}{\Lambda_C+\Lambda_A}$ gram equivalents of negative ion will go from the dilute to the concentrated side. Let P be the osmotic pressure of the positive and negative ions in the concentrated solution, and P' that of those in the dilute solution. The maximum electrical work work to be done by the process, then, will be,

$$\frac{\Lambda_C}{\Lambda_C+\Lambda_A}RT\log_e\frac{P}{P'}-\frac{\Lambda_A}{\Lambda_A+\Lambda_C}RT\log_e\frac{P}{P'}=\frac{\Lambda_C-\Lambda_A}{\Lambda_A+\Lambda_C}RT\log_e\frac{P}{P'},$$

and this must be equal to FE for the process going in this way, i.e., to the electrical work done at the surface of contact of the two solutions. Since R is in calories this value will also be expressed in calories. To transform it into electrical units it is only necessary to divide through by 23,074. This relation was derived and tested experimentally by Nernst (Zeit. f. phys. Chem., 4, 129, 1888), who found it to hold true within the experimental error.

From the above, we should expect that a weaker solution of an acid or base, when superimposed on a stronger one, would show the polarity of the faster moving ion. In other words in diffusing through the solution the faster ion would impart its polarity to the weaker solution. With acids, indeed, we do observe that the dilute solution is positive, while with bases it is negative; and this is in accord with our previous observations that H^+ and OH^- are the ions possessing the greatest mobility or velocity. This process does not result in a complete separation of the ions nor even in more than a very slight one, for it must be remembered that the two kinds of electricity attract one another, the consequence of which is that the speed of the faster-moving ions will be decreased, while that of the slower will be increased.

This same method of reasoning will also enable us to understand the action of the cell arrangement

Concentrated amalgam of the metal *M*.	Water solution of a salt of the metal *M*.	Dilute amalgam of the metal *M*.

In this case the passage of 96,494 coulombs will cause 1 gram equivalent of the metal *M* to go from the concentrated side to the dilute, and, if there are n_e equivalents to the mole, the maximum work per equivalent will be

$$\frac{1}{n_e} RT \log_e \frac{c_1}{c_2},$$

where c_1 and c_2 are the concentrations of the metal *M* in the amalgams. Again, here, if this expression is so transformed as to give electrical units instead of calories, by division by

23,074, it will give the value of E, the electromotive force in volts of the cell operating in this way.

And the same is true for cells with electrodes of the same soluble metal and two concentrations of a solution of a salt or salts of that metal. Consider, for example, the cell

$$\mathrm{Cu}\;\begin{array}{|c|c|}\text{dilute} & \overset{\longrightarrow}{\text{concentrated}} \\ \mathrm{CuSO_4} & \mathrm{CuSO_4}\end{array}\;\mathrm{Cu}.$$

By passing a current through this cell in the direction of the arrow the following changes will take place:

1. For each 96,494 coulombs of electricity 1 gram equivalent of copper will dissolve from the electrode in the dilute solution, i.e., will be transformed from the metallic to the ionic state.

2. At the boundary of the two solutions the process described above will take place; and

3. One gram equivalent of Cu^{++} ion will be deposited from the concentrated solution upon the electrode.

As the result of processes (1) and (3) 1 gram equivalent of Cu^{++} ion will go from the concentrated to the dilute solution. The maximum work of this process, then, for each 96,494 coulombs will be

$$\frac{RT}{n_e}\log_e\frac{P_1}{P_2},$$

where n_e is the valence of the metal and P_1 and P_2 are the osmotic pressures of the Cu^{++} ion in the two solutions.

By the second process (contrast with direction of current in the case above) we have as the work

$$\frac{RT}{n_e}\cdot\frac{\Lambda_A-\Lambda_C}{\Lambda_A+\Lambda_C}\log_e\frac{P_1}{P_2}.$$

This second value is usually so small, when compared to the other, that it may generally be neglected, and the two differences of potential between the electrodes and the solutions measured separately.

Neglecting the difference of potential between the liquids, then, we have

$$E=\frac{RT}{n_eF}\log_e\frac{P_1}{P_2},$$

or, including the potential difference between the solutions,

$$E=\frac{RT}{n_eF}\cdot\frac{2\Lambda_A}{\Lambda_A+\Lambda_C}\log_e\cdot\frac{P_1}{P_2},$$

i.e., the sum of the two, where R must be given in electrical units, if E is to be expressed in volts.

By separating the amount of work $\frac{RT}{n_e}\log_e\frac{P_1}{P_2}$ into two portions, so that each will give the maximum work at an electrode, we can write

$$\frac{RT}{n_eF}\log_e\frac{P_M}{P_2}-\frac{RT}{n_eF}\log_e\frac{P_M}{P_1},$$

where P_M is a constant for any one metal at the same temperature, in the same solvent, and is called the *electrolytic solution pressure.* The portions containing the expressions $\log_e\frac{P_M}{P}$ will then give the difference of potential of copper in dilute copper sulphate and copper in concentrated copper sulphate.

The *electrolytic solution pressure* assumed to exist in this way is analogous to the ordinary solution pressure which we have already considered, except in this case it is for the solution of a metal or any other element, i.e., is the pressure with which the element tends to attain the ionic state.

When we consider a stick of metal in a solution of one of its salts, we have, if P_M is the electrolytic solution pressure, and P is the osmotic pressure of the metal ion in the solution, three possibilities:

1. $P_M = P$.
2. $P_M > P$.
3. $P_M < P$.

We shall now consider briefly these three cases.

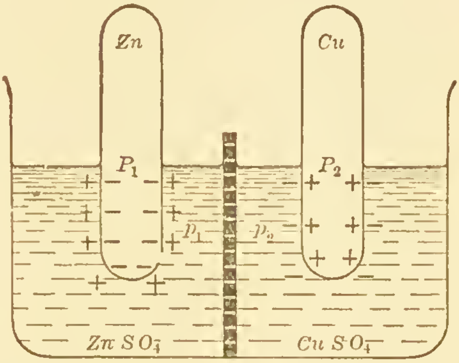
1. $P_M = P$. We shall observe no action in this case, since the two opposing pressures are equal and consequently cancel.

2. $P_M > P$. This is the case with Zn. Zn^{++} ion will go from the electrode into the solution, taking with it positive electricity. This process will take place only to a very slight degree, however, for it would increase the positive charge of the solution, and cause it to become greater than the negative. This positive matter around the electrode when once formed must at once be attracted back to the electrode, for that has become negatively charged owing to the loss of positive ion. Finally, then, we have the metal negative against the solution, and the electrode will be surrounded by what is known as a Helmholtz double layer, in this case a layer of positive ion on a negative plate. If positive electricity is supplied now from another source to the metal, the double layer is broken up and more Zn will go into solution in the ionic form, but as soon as the supply of electricity is stopped, the double layer will again be formed.

3. $P_M < P$. This is true for Cu. A stick of copper in a solution of one of its salts will have Cu^{++} ion from the solution deposited upon it, since the pressure toward the electrode is greater than that away from it. This Cu^{++} brings positive electricity with it, consequently the metal is positive against its solution. The double layer will also be formed here, for

the positive charge on the metal will attract negative ion from the solution. In this case, however, the double layer will be broken up when electricity is conducted away from the electrode, for then the Cu^{++} ion will again precipitate and continue to do so until $P=P_M$, when all action will cease. Since 1 gram equivalent of any ion carries with it 96,494 coulombs of electricity, the amount of metal going into or out of solution may be infinitesimal and yet cause the production of a measurable amount of electricity.

The relations of Cu and Zn in their respective solutions are shown in the figure.

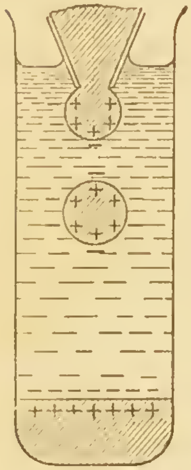


The double layer is formed on both. Until the Cu and Zn are connected by a wire the equilibrium as it is will be undisturbed. When they are connected, a current will go through the wire from Cu to Zn, i.e., Zn^{++} ion will go into the solution, depositing an equivalent amount of Cu^{++} ion upon the copper plate. The electromotive force will then depend on the difference between the two values of P_M, if P is the same on both sides; and the amount of current will depend upon the number of gram equivalents of Zn dissolved and of Cu precipitated.

It is the ratio $\frac{P_M}{P}$, as will be seen, that regulates the behavior of an electrode toward a solution of its salt. If the counter-osmotic pressure P is equal to P_M, the electrode does not dissolve; if the counter pressure is greater, ionized metal is deposited upon it; while if the pressure is less, the metal goes into solution as ion.

If, for example, we add sufficient KCN to the Cu side of the Daniell cell, we find that the copper actually dissolves, while zinc on the other hand is deposited. Here then the ratio $\frac{P_M}{P}$, which was smaller for copper than for zinc, has now become greater than that. In other words, the osmotic pressure of the Cu^{++} ion has decreased by the formation of the complex $CuCN_2^{=}$, into which all copper dissolving is transformed.

The presence of a layer of ion around the charged metal has been proven by Palmaer (Wied. Ann., 18, 257, 1899) by an arrangement shown in the figure.



Drops of mercury are allowed to fall into weak solution containing mercurous ion, metallic mercury being in the bottom of the tube containing the solution. If now the double layer theory is true, the drops of Hg as they form should have the charge from the amount of Hg_2^{++} ion which has been deposited upon them, and these positively charged drops should then attract negative ion, which would form on each a double layer. When such a drop reaches the mercury at the bottom it will join with that, forming once more Hg_2^{++} ion and releasing those of the negative radical, and the concentration of mercury salt should be greater at the bottom than at the top. Palmaer's experiments showed this difference in concentration to actually exist.

Experiment has shown that the metals Na, K, . . . , etc., up to Zn, Cd, Co, Ni, and Fe are always negative against their solutions, i.e., $P_M > P$.

The noble metals, on the contrary, are positive against their solutions, although in some few cases it is possible to get a solution in which $P_M > P$. In general, though, for the noble metals $P_M < P$.

A negative element has exactly the same action as a positive one, except that, in general, as far as is known, $P_M > P$. Here, although $P_M > P$, the electrode is positive against the solution, for the negative ion formed from the electrode leaves positive electricity on the electrode.

In general, the electrolytic solution pressure depends upon the temperature, the nature of the solvent, and the concentration of the substance in *the electrode*, if this is an alloy or amalgam.

General mathematical expression of the osmotic theory of the cell.—It is possible from the above conception of solution pressure to derive the formula giving the value of the difference of potential of a single electrode of any metal against a solution of one of its salts. This will depend upon the osmotic pressure of the metal ion working in the one direction and upon the electrolytic solution tension working in the other. Since the ion goes from one pressure to the other, a certain amount of work is done and this amount must always be the same no matter in what form it appears, i.e., whether electrical or osmotic.

When 1 mole of a monovalent ion is transferred from the pressure P_M to the pressure P, the osmotic work done is equal to

$$\int_P^{P_M} RT\frac{dP}{P} = RT\int_P^{P_M}\frac{dP}{P},$$

from which, by integration, we obtain

$$RT \log_e \frac{P_M}{P}.$$

The corresponding electrical work, however, is EF where E is the difference of potential between the metal and solution and F is the amount of electricity carried by 1 gram equivalent of ions. We have then

$$EF = RT \log_e \frac{P_M}{P},$$

or

$$E = \frac{RT}{F} \log_e \frac{P_M}{P},$$

from which we see that if $P_M = P$, $E = 0$.

E for 1 mole of a monovalent ion (i.e., for 1 equivalent) is equal to 96,494 coulombs. We must, however, express both sides of the equation in electrical units. Since $R = 2$ cals., the right side of the equation must be divided by 0.2391 $\left(= \frac{23074}{96494},\right.$ see page 389) in order to obtain our result in electrical units. We have then

$$96494 \times E(\text{volts}) = \frac{2}{0.4343 \times 0.2391} T \log \frac{P_M}{P},$$

or

$$E = 0.058 \log \frac{P_M}{P} \text{ volts at } 17^\circ \text{ C.}$$

For a divalent element we must multiply F by 2; hence, in general, if n_e is the valence of the metal, we have

$$E = \frac{0.0002}{n_e} T \log \frac{P_M}{P} \text{ volts},$$

or for negative ions

$$E = -\frac{0.0002}{n_e} T \log \frac{P_M}{P} = \frac{0.0002}{n_e} T \log \frac{P}{P_M} \text{volts}.$$

If we consider a cell composed of two metals, each present in a solution of one of its salts, the difference of potential may arise, (1) at the place of contact of the two metals, (2) at the place of contact of the two solutions, and (3) and (4) at the points of contact of the two electrodes with their solutions. The first can be entirely neglected provided the temperature remains constant. The second, as was mentioned above, is always small, so that we shall have to consider here only (3) and (4). At 17° the electromotive force of the cell will be, then,

$$E = \epsilon_1 - \epsilon_2 = \frac{0.0579}{n_e} \log \frac{P_{M.1}}{P_1} - \frac{0.0579}{n_e} \log \frac{P_{M.2}}{P_2} \text{ volts,}$$

the minus sign being used because an ion is formed on the one side, and consequently must disappear upon the other, for there must always be an equivalent amount of positive and negative ions in the solution.

The measurement of the potential difference between a metal and a solution.—The method in use for the determination of differences of potential is based upon the use of a normal electrode, i.e., an electrode in a solution of one of its salts, of which the potential difference is known. Making up a cell by combining this electrode with the one to be measured, it is possible, then, from observations of the resulting electromotive force, to find the value of the unknown potential difference. The original measurement of the potential difference of the normal electrode was made by forming a cell with this and another electrode, having a potential of zero against its solution. The electromotive force of this combination, then, is identical with the potential difference to be found. Such an electrode with zero potential, the so-called "dropping electrode," is formed when mercury flows into a solution of an electrolyte (KCl), for any differences of potential existing between the mercury and solution must eventually be eliminated by the continually dropping mercury.

The electrodes in general use are made up according to one of the two following schemes:

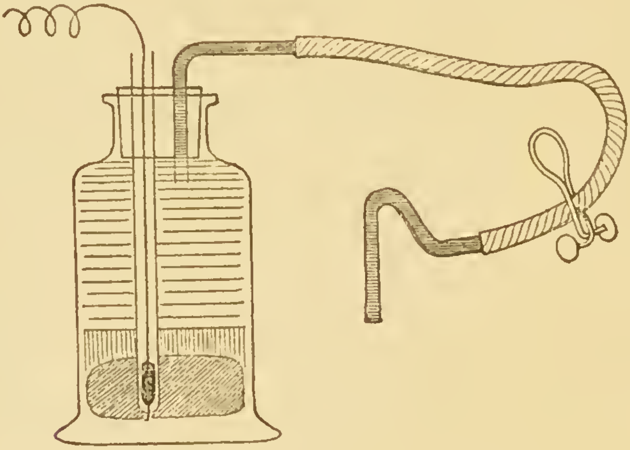
HgCl in equivalent normal KCl/Hg,

or

HgCl in 0.1 equivalent normal KCl/Hg;

the former giving a difference of potential of −0.56 volt, the latter of −0.613, both at 18°. The sign in each case here refers to the solution, i.e., the solution is negative against the mercury.

The figure shows the form of the cell. The siphon tube is so arranged that it is always kept full of the KCl solution.



This dips into the liquid of the other electrode, provided they form no precipitate. In case they do, a molar solution of KNO_3 is used, into which the siphons from the two electrodes dip. The advantage of using KNO_3 as a connector is that the mobilities of K^+ and NO_3^- ion are nearly the same; hence the passage of the current produces no change in the concentration at the two sides and consequently gives rise to no difference of potential.

An example of the use of this electrode in measuring the difference of potential of any other single electrode is given by the following: For a combination in the form

$$\mathrm{Zn}-\text{equivalent } \mathrm{ZnSO_4}-\text{equivalent } \mathrm{KCl\ HgCl}-\mathrm{Hg},$$

i.e., for

$$\mathrm{Zn} \text{ in equivalent } \mathrm{ZnSO_4},$$

against the normal electrode, we find $E=1.08$ volts, the current going from Hg to Zn through the wire. The total electromotive force of the cell, then, is given by the equation

$$E=(\epsilon_1-\epsilon_2)=\frac{RT}{2F}\log_e\frac{P_{M.1}}{P_1}-\frac{RT}{F}\log_e\frac{P_{M.2}}{P_2},$$

where $P_{M.1}$ and P_1 refer to the Zn, and $P_{M.2}$ and P_2 to the Hg, for that is the only arrangement which would make E positive. We have then

$$1.08=\frac{RT}{2F}\log_e\frac{P_{M_1}}{P_1}+0.56,$$

$$\frac{RT}{2F}\log_e\frac{P_{M_1}}{P_1}=(1.08-0.56)=0.52 \text{ volt};$$

i.e., Zn is negative against a molar solution of its sulphate and gives a difference of potential of 0.52 volt. *The sign always refers to the difference of potential of the electrolyte as against the electrode.* Thus, -1 means that the solution is negative and the metal positive, and *vice versa*.

In the case of

$$\mathrm{Cu}-\text{equivalent } \mathrm{CuSO_4}-\text{equivalent } \mathrm{KCl\ HgCl}-\mathrm{Hg},$$

we find $E=0.025$ volt, the current in the wire going from Cu to Hg. We have here, since the current goes from Hg to Cu in the solution

$$E=\frac{RT}{F}\log_e\frac{P_{M.2}}{P_2}-\frac{RT}{2F}\log_e\frac{P_{M.1}}{P_1},$$

or

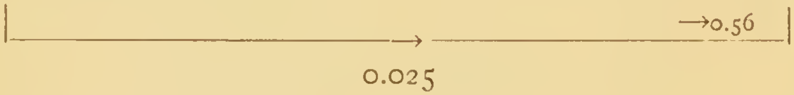
$$0.025=-0.56-\frac{RT}{2F}\log_e\frac{P_{M.1}}{P_1},$$

$$\frac{RT}{2F}\log_e\frac{P_{M.1}}{P_1}=-0.025-0.56=-0.585;$$

i.e., the electrode of Cu is positive, with a difference of potential against the electrolyte equal to 0.585 volt.

The method of calculation is shown more clearly, perhaps, by the following diagram:

Cu – equivalent $CuSO_4$ . . . . . . HgCl in equivalent KCl – Hg,



which shows that the copper side must be more positive than the mercury by 0.585 volt if it is to be positive in the combination and give it an electromotive force of 0.025 volt.

The heat of ionization.—Knowing the difference of potential existing between a metal and a solution, and its rate of change with a variation in the temperature, it is possible from the formula on page 420 to find the heat of ionization of the metal. We found there that

$$\text{electrical energy}=\text{chemical energy}+FT\frac{dE}{dT},$$

or

$$E=\frac{\text{chem. eng.}}{F}+T\frac{dE}{dT}$$

The term "chem. energ." here, is the heat produced when 1 gram equivalent of the metal goes from the metallic to the ionic state, and its value is given by the formula

$$\text{chem. energ.} = \left(E - T\frac{dE}{dT}\right) 23074 \text{ cals.},$$

where the term "chem. energ." is identical with the heat of ionization per equivalent.

For copper in copper acetate (normal) solution at 17°, $E=0.6$, and $\frac{dE}{dT}=0.000774$, while $\frac{dE}{dT}$ for copper in copper sulphate solution is 0.000757, i.e., an average value of $\frac{dE}{dT}$ of 0.000766 volt; hence the heat of ionization of copper is 8722 cals. per gram equivalent, or 17,444 cals. per mole. It was in this way that the value for hydrogen was determined for use in the table given on page 245.

Concentration-cells. *a. In which the electrodes have different concentrations.*—If the electrodes are made of two amalgams of the same metal, in solutions of salts of this metal the electromotive force of the cell is given by the formula

$$E = \frac{0.0002}{n_e} T \log \frac{P_{M.1}}{P_1} - \frac{0.0002}{n_e} T \log \frac{P_{M.2}}{P_2} \text{ volts.}$$

If the two solutions have the same concentration of metal ion, then $P_1 = P_2$, and we have

$$E = \frac{0.0002}{n_e} T \log \frac{P_{M.1}}{P_{M.2}} \text{ volts,}$$

when $P_{M.1}$ and $P_{M.2}$ are the electrolytic solution pressures of the two electrodes with respect to the dissolved metal.

Amalgams when dilute may be considered as solutions, in which the mercury acts as the solvent; consequently the osmotic pressure of the metal in the amalgam will be proportional to the electrolytic solution pressure of the electrode. Since in all solutions the osmotic pressure is proportional to the concentration, we may substitute for the electrolytic solution pressures the proportional terms, the concentrations in equivalents of the metal in the two electrodes. We obtain then

$$E = \frac{0.0002}{n_e} T \log \frac{c_1}{c_2} \text{volts.}$$

This formula was proven experimentally by G. Meyer (Zeit. f. phys. Chem., 7, 377, 1891;) see also Cady (J. Phys. Chem., 2, 551–564, 1898); and Richards and Forbes (Carnegie Publication No. 56, 1907), some of whose results for zinc amalgams in a $ZnSO_4$ solution are given in the table below:

T	c_1	c_2	E (obs.), volts	E (calc.), volts
11°.6	0.003366	0.00011305	0.0419	0.0416
18°	0.003366	0.00011305	0.0433	0.0425
12°.4	0.002280	0.0000608	0.0474	0.0445
60°	0.002280	0.0000608	0.0520	0.0519

The results obtained by Meyer also proved the formula to hold for copper amalgams in $CuSO_4$, etc., solutions.

We have assumed the metals to dissolve in mercury in the monotomic form in this case, and the assumption is upheld by our results, not only by this method, but also by others.

If Zn had been present in the diatomic form in the mercury, our equation would have had a different value. For the movement of the same amount of ionized material as before, we should have had, then, the osmotic work equal to

$$\frac{1}{2} \cdot \frac{RT}{0.4343} \log \frac{c_1}{c_2},$$

and since the electrical work would have been the same as before, i.e.,

$$2\times 96494\ E,$$

we should have had

$$E=\frac{1}{2}\cdot\frac{0.0002}{2}T\log\frac{c_1}{c_2}\text{ volts;}$$

i.e., the electromotive force would have been one-half what we have found it to be.

The electromotive force is found, then, to be dependent only upon the concentration of the metal in the amalgams and its valence, and not upon the nature of the metal itself. The mercury has no effect so long as the metal dissolved in it gives the larger electromotive force.

Another example of the electrodes having different electrolytic solution pressures, owing to differences of concentration, is given by cells of the type of the Grove gas-battery in an altered form. The electrodes are of plantinized platinum, in which the gas is absorbed under different pressures, and are placed partly in the liquid and partly in gas of corresponding (partial) pressure. Such an electrode is to be considered as a perfectly reversible gas electrode,* i.e., one from which the material absorbed as a gas is given up in the ionized state, or when deposited from the ionic state is transformed into gas; for the metal acts simply as a conductor, as has been shown experimentally by the use of different metals, the same result is always obtained. In this way reversible gaseous electrodes of all kinds can be made. Oxygen as an electrode, however, gives off OH^- ion, and absorbs O, when the OH^- ion gives up its charges to it, forming H_2O and O.

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* The electrolytic solution pressure here of the gas electrode is proportional to the nth root of the gaseous pressure, where n is the number of combining weights in one formula weight of the gas.

If we have two hydrogen gas electrodes, under different pressures, in contact with a liquid containing H^+ ion, we shall obtain a certain electromotive force. This may be calculated in two ways, as we did in the case of amalgams. In the second way, however, the process is slightly different, since one mole of H gas forms two equivalents of monovalent ion (page 207). The osmotic work here is equal to

$$\frac{RT}{0.4343} \log \frac{P_{M,1}}{P_{M,2}},$$

as before. The electrical work, however, which corresponds to this is now $2FE$, for $H_2 = 2H^+$, hence

$$E = \frac{RT}{2F(0.4343)} \log \frac{P_{M,1}}{P_{M,2}},$$

i.e., we have 2 in the denominator notwithstanding that the gas is monovalent.

b. Different ionic concentrations.—In this type of cell we assume the electrodes to be of the same metal, but dipping into solutions which possess different ionic concentrations of the metal. An example is given by the arrangement

$$Ag(AgNO_3 \text{ conc.}) - (AgNO_3 \text{ dilute})Ag,$$

where the liquids are connected by tubes stuffed with lamp wicking, through an intermediate vessel containing a solution of potassium nitrate.

From the general equation we have here

$$E = \frac{RT}{F} \log_e \frac{P_{M,1}}{P_1} - \frac{RT}{F} \log_e \frac{P_{M,2}}{P_2}.$$

Or, since $P_{M,1} = P_{M,2}$,

$$E = \frac{RT}{F} \log_e \frac{P_1}{P_2},$$

where P_1 is the osmotic pressure of the Ag^+ ion on the concentrated side and P_2 that on the dilute side.

From this we see that the electromotive force of such a cell depends only upon the ratio of the concentrations and temperature, and not at all upon the actual concentrations, which was found also to be true experimentally by Nernst (l.c. page 118).

Since the osmotic pressure is proportional to the concentration, we may substitute the latter for the former and obtain

$$E = \frac{RT}{n_e F} \log_e \frac{c_1}{c_2}$$

The concentration of Ag^+ ion in a 0.01 molar solution of $AgNO_3$ is 8.71 times as great as that in a solution which is 0.001 molar (not 10 times), hence the electromotive force (at 18°) of a cell made up of Ag in these two concentrations of $AgNO_3$ should be

$$E = 0.0002 \times 291 \log 8.71 = 0.054 \text{ volt},$$

while 0.055 volt was found by experiment.

Since at 18° C. we have

$$E = \frac{0.0582}{n_e} \log \frac{c_1}{c_2} \text{ volts},$$

a concentration ratio of the ions equal to 10, would give $E = 0.0582$ volt for a monovalent ion, or 0.0291 volt for a divalent one.

This class includes all cells made up of solutions containing different ionic concentrations of the same metal, *both* electrodes being of that metal. In case the contact of the two liquids causes the formation of a precipitate, another solution is used between, the two being connected by small siphons.

Dissociation by aid of the electromotive force.—Since for concentration-cells we have the formula

$$E=\frac{0.0002}{n_e}T\log\frac{c_1}{c_2}\text{ volts,}$$

i.e., for monovalent metals

$$\log\frac{c_1}{c_2}=\frac{E}{0.0002T},$$

we can find the ionic concentration of the metal on the one side provided that on the other is known.

An example of this is the cell as given by Morgan:

$$\mathrm{Ag}-\frac{\text{normal}}{10}\mathrm{AgNO_3}-\mathrm{KNO_3}-\frac{\text{normal}}{20}\mathrm{KAgCN_2}-\mathrm{Ag},$$

which gives an E.M.F. of 0.542 volt, the Ag in $AgNO_3$ being the positive pole. If the 0.1 normal solution of silver nitrate is considered as 85 per cent ionized, the concentration of Ag^+ ion, i.e. c_1, will be 0.085 mole per liter, and since $T=273+17^\circ=290$, we have

$$\log\frac{c_1}{c_2}=\frac{0.542}{0.0002\times290},$$

from which $c_2=3.83\times10^{-11}$

i.e., a 0.05 normal solution of $KagCN_2$ contains 3.83×10^{-11} mole per liter of silver ion.*

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* It is always best here, to avoid mathematical difficulties, to find the actual value of the ratio $\frac{c_1}{c_2}$ first, eliminating logarithms, and then to find the value of c_2, for example, from the known c_1, by arithmetical means.

This method was devised by Ostwald, *and is one of the most delicate known, for the more dilute the one solution is, i.e., the smaller the concentration of its metal ion, the greater is the electromotive force of the cell, and the greater the accuracy of the result.*

Another typical cell of this kind is

$$\mathrm{Ag} - \frac{n}{10}\mathrm{AgNO_3} - \mathrm{KNO_3} - \frac{n}{10}\mathrm{KCl\ AgCl} - \mathrm{Ag},$$

which was used by Goodwin to determine the solubility of AgCl.

In a saturated water solution of AgCl we may assume without error that the dissociation is complete. The solubility product will then be

$$c_{\mathrm{Ag}^+} \times c_{\mathrm{Cl}^-} = s.$$

Since in a pure water solution of AgCl, $\mathrm{Ag}^+ = \mathrm{Cl}^-$, the square root of s, s being determined under any conditions at constant temperature, will give directly the concentration of Ag^+ (or Cl^-) in the solution. And, if complete ionization may be assumed, this is equal to the solubility of AgCl under these conditions.

For example, if we find the electromotive force of the cell

$$\mathrm{Ag} - \mathrm{AgCl} - \mathrm{KCl} - \mathrm{AgNO_3} - \mathrm{Ag},$$

where c_{Cl^-} on the left in the KCl, and c_{Ag^+}, on the right in the $\mathrm{AgNO_3}$ solution, are known, we can calculate c_{Ag^+} on the left, and consequently s and the solubility of AgCl.

Goodwin (Zeit. f. phys. Chem., 13, 577, 1894) found, when the concentration of $\mathrm{AgNO_3}$ and KCl was 0.1 normal, an average electromotive force of 0.45 volt at 25.° By conductivity measurement at 25° we find that α for N/10 $AgNO_3$ is 0.82, so that we have

$$\log \frac{0.82 \times 0.1}{c_2} = \frac{0.450}{0.0002 \times 288},$$

or

$$c_2 = 2.31 \times 10^{-9},$$

i.e., Ag^+ ion is present in a 0.1 normal KCl solution saturated with AgCl to a concentration of 1.94×10^{-9} moles per liter in the presence of 0.085 mole of Cl ion from the KCl, for the N/10 solution is 85 per cent ionized. The solubility product s must then be equal to

$$c_{Ag} \times c_{Cl} = s_{AgCl},$$

i.e., to $$2.3 \times 10^{-9} \times 0.085 = s = 1.96 \times 10^{-10},$$
and

$$\sqrt{s} = 1.4 \times 10^{-5};$$

i.e., AgCl in a saturated water solution at 25°, where c_{Ag^+} must be identical with c_{Cl^-}, is present to a concentration of 1.4×10^{-5} moles per liter.

A cell of this sort may be arranged with bromides, iodides, etc., in place of the chlorides, which was also done by Goodwin, and the solubility of AgBr and AgI determined.

Another illustration of this method of determining dissociation is furnished by Ostwald's arrangement for determining the dissociation constant for water. The scheme is a gas-cell in the form

$$H - \text{Acid} \ldots\ldots\ldots \text{Base} - H,$$

when the two H electrodes have the same solution pressure. The electromotive force of such a cell, deducting that caused by the contact of the two solutions, for molar solutions at 17° C., is

$$E = 0.058 \log \frac{c_1}{c_2}.$$

Here, contrary to the case for electrodes of different gaseous concentration, the 2 does not appear in the denominator (page 440), for that factor simply refers to the process taking place between the electrode and the gas. In this case the electrodes remain constant and the same, and only the osmotic pressures of the H^+ ion is to be considered. By experiment $E = 0.81$ volt; hence, since $c_1 = 0.8$ (i.e., the normal acid is 80% dissociated),

$$\frac{c_1}{c_2} = 10^{14},$$

or

$$c_2 = 0.8 \times 10^{-14}.$$

Since this is the concentration (in terms molar) of the H^+ ion in the base, and the concentration of the OH^- ion existing in equilibrium with it is 0.8, the ionic product for water must be

$$s_{H_2O} = 0.8 \times 0.8 \times 10^{-14}.$$

Since H_2O dissociates into H^+ and OH^+, the concentration of H^+ and OH^- ion in pure water is the same and is, therefore, equal to

$$\sqrt{(0.8)^2 \times 10^{-14}} = 0.8 \times 10^{-7} = c_{H^+} = c_{OH^-} \text{ in } H_2O.$$

From the conductivity also, at this temperature, Kohlrausch found

$$c_{H^+} = c_{OH^-} = 0.8 \times 10^{-7}.$$

It would be possible in this case to use oxygen electrodes, by which the same final result would be obtained, but platinum black absorbs very little oxygen, so that the results are not as certain as with hydrogen.

For details as to the use of the hydrogen gas electrode for the calculation of concentrations of H^+ ion, see Hilderbrand (Jour. Am. Chem. Soc., 35, 847–874, 1913) and Loomis and Acree (Am. Chem. J., 46, 585, and 621, 1911).

For the measurement of the concentration of the ion of mercury the normal electrode serves as the basis. The concentration of Hg_2^{++} ion in the normal electrode has been found to be 3.5×10^{-18} mole per liter (Ley and Heimbucher, Zeit. f. Electrochem., 10, 303, 1904). Since $\frac{Hg_2^{++}}{Hg^{++}}=120$, in the presence of metallic mercury, according to Abel (Zeit. f. anorg. Chem., 26, 377, 1901), it is possible to find the concentration of Hg^{++} in the normal electrode; it is equal to 2.9×10^{-20} mole per liter. By measurements of the electromotive force of a combination of mercury in a solution containing Hg^{++} or Hg_2^{++} ions, with the normal electrode we can thus determine the concentration of these ions. For further details as to this, see Sherrill and Skowrouski, J. Am. Chem. Soc., 27, 30, 1905.

Electrolytic solution pressure.—It is possible from the potential difference between a metal and its salt solution to calculate the electrolytic solution pressure of the metal, in atmospheres. The equation is that for the potential difference at a single electrode, viz.,

$$\epsilon=\frac{RT}{n_eF}\log_e\frac{P_M}{P},$$

or at 17°

$$\log P_M=\frac{\epsilon n_e}{0.0002T}+\log P.$$

If we use normal solutions, P is equal to $22.4\times\frac{290}{273}$ atmospheres, if the salt is completely ionized. The pressure of the ion, in case the salt is not completely dissociated, is then easily found from its degree of ionization (i.e., $\alpha \times 22.4\frac{290}{273}$ atmospheres). Since ϵ can be determined, the value for P_M can be found for all metals. In the following table the values in atmospheres, as determined by Neumann, are given.

These values it must be remembered are merely symbolical, for the gas laws may not be applied to such an extent. The relation between these numbers, however, are the experimentally determined relative effects of the metals, as a glance at the formula used in a cell arranged as on page 437 will show.

ELECTROLYTIC SOLUTION PRESSURES OF METALS

	Atmospheres
Zinc	9.9×10^{18}
Cadmium	2.7×10^{6}
Thallium	7.7×10^{2}
Iron	1.2×10^{4}
Cobalt	1.9×10^{0}
Nickel	1.3×10^{0}
Lead	1.1×10^{-3}
Hydrogen	9.9×10^{-4}
Copper	4.8×10^{-20}
Mercury	1.1×10^{-16}
Silver	2.3×10^{-17}
Palladium	1.5×10^{-36}

Cells with inert electrodes.—Elements of this type have electrodes in solutions which do not contain the ions of the electrodes. Such cells are also known as *oxidation and reduction cells*. An example is given by the arrangement

$$\text{plat.Pt} - \text{FeCl}_3\text{sol} \ldots\ldots \text{SnCl}_2\text{sol.} - \text{plat.Pt.}$$

The Sn^{++} ion goes over into the Sn^{++++} ion, taking up the electricity set free by the transformation of Fe^{+++} ion into Fe^{++}. The Fe side, then, is positive and the Sn side negative.

The current in these cells is due to the oxidation on the one side and the reduction on the other. An oxidizing substance (i.e., one which is reduced) is any substance from which negative ions are formed or upon which positive ions give up their charges. A reducing substance is one in which negative ions are given up or positive ions formed.

D. ELECTROLYSIS AND POLARIZATION

Decomposition values.—We must now consider the processes which take place when a current is passed through a solution from electrodes which are not affected by the liquid, i.e., inert ones, as platinum, gold, carbon, etc. The current causes the deposition of the positive and negative ions on the electrodes. If the primary current is disconnected at any time and the poles of the decomposition-cell connected with a galvanometer, we observe a current in the opposite direction which becomes weaker and weaker, until it finally disappears entirely. This is called the *current of polarization*, and its electromotive force is called *the electromotive force of polarization*, and is caused by the tendency of the substance precipitated upon the electrode to go back into solution in the ionic state.

It has been found that a certain minimum of electromotive force is necessary to cause the steady electrolysis of any solution. If the electromotive force used is smaller than this, the current goes through for an instant and then ceases; but at the electromotive force of polarization or above it, the process goes on steadily. This was found by Le Blanc, who determined the minimum values for a large number of liquids and solutions. The table below gives these values for normal solutions of the salts which separate metals.

DECOMPOSITION VALUES FOR SALTS IN VOLTS

$ZnSO_4 = 2.35$
$Cd(NO_3)_2 = 1.98$
$ZnBr_2 = 1.80$
$NiSO_4 = 2.09$
$NiCl_2 = 1.85$
$Pb(NO_3)_2 = 1.52$

$AgNO_3 = 0.80$
$CdSO_2 = 2.03$
$CdCl_2 = 1.88$
$CoSO_4 = 1.94$
$CoCl_2 = 1.78$

Judging from the results for $Cd(NO_3)_2$ and $CdSO_4$, it would seem in general that the values for the nitrates and sulphates of the same metal are nearly the same.

The following tables contain the values for acids and bases. Here there is a certain maximum, which is reached by many and exceeded by none, which is about 1.70 volts.

DECOMPOSITION VALUES FOR THE ACIDS IN VOLTS

Sulphuric	=1.67	Dextrotartaric	=1.62
Nitric	=1.69	Pyrotartaric	=1.57
Phosphoric	=1.70	Trichloracetic	=1.51
Monochloracetic	=1.72	Hydrochloric	=1.31
Dichloracetic	=1.66	Oxalic	=0.95
Malonic	=1.72	Hydrobromic	=0.94
Perchloric	=1.65	Hydriodic	=0.52

DECOMPOSITION VALUES FOR THE BASES IN VOLTS

Sodium hydroxide	=1.69	N/4
Potassium hydroxide	=1.67	N/2
Ammonium hydroxide	=1.74	N/8
Methylamine N/4	=1.75	
" N/2	=1.68	
" N/8	=1.74	

The alkalies and alkaline earths when combined with the largely dissociated acids, i.e., those with decomposition values of about 1.70 volts, show approximately the same value, viz., 2.20 volts. The chlorides, bromides, and iodides have lower values, which are independent of the alkali metal.

It will be observed that all the acids and bases with the maximum value give off hydrogen and oxygen upon electrolysis. Those with the lower values, which in more dilute solutions give off oxygen and hydrogen, also reach this maximum value. Thus for hydrochloric acid at different dilutions we have:

DECOMPOSITION VALUES FOR HCl

Concentration	*E*	Concentration	*E*
2 normal	=1.26	1/16 normal	=1.62
1/2 "	=1.34	1/32 "	=1.69
1/6 "	=1.41		

At the dilution N/32 gaseous hydrogen and oxygen are given off instead of hydrogen and chlorine, as at the strength of 2 normal, and the maximum is reached.

All the above results are for platinum electrodes. For gold the values are slightly different, but the relation remains the same.

Theory of polarization.—The process taking place upon an electrode during electrolysis has been studied by Le Blanc, who has been able to make the action quite clear. He measured the difference of potential between the cathode and its solution after the passage of the current, varying the electromotive force from 0 up to the decomposition value of the solution. At the decomposition value he found the potential difference to be the same as that exhibited by the solution in which is placed a stick of the metal. Thus a normal solution of $CdSO_4$ is decomposed steadily at 2.03 volts, at which the difference of potential between the cathode and solution is found to be $+0.16$ volt. A stick of cadmium in a normal solution of $CdSO_4$ gives an electromotive force equal to $+0.16$ volt, i.e., the metal is negative. For some solutions this difference of potential between electrode and solution is found to be given without the maximum being reached. This is true for $AgNO_3$, which decomposes at 0.70 volt. The reason for this is the negative solution pressure of the Ag, which causes Ag^+ ion to be deposited upon the metal, even without the current.

When an indifferent electrode is placed in a salt solution, a small amount of ion must precipitate upon it; otherwise, from the equation

$$E=\frac{RT}{n_eF}\log_e\frac{P_M}{P},$$

E will be infinite, since $P_M=0$. Metal ion will then separate upon the electrode until the tendency for the deposited metal to go into solution in the ionic form just compensates the separating force. In this way the electrode will be charged positively, and the solution negatively, so that there will be between them a certain difference of potential. The value of this difference will depend upon the amount of the metal upon the electrode, and will not necessarily be as large as that for the massive metal (compare with concentration of H in a platinum-black electrode). If we now connect the cell with a primary cell at a low electromotive force, more metal will be deposited, but this will increase the apparent value of P_M, so that no more deposition will take place at that electromotive force. If the potential is then increased, the apparent value of P_M will again increase and further deposition will be prevented. Finally, when the electromotive force used is such that this increasing P_M factor attains its maximum value, i.e., that which the massive metal possesses, then the deposition will take place steadily. Here we assume the osmotic pressure of the metal ion to remain constant. For strong currents this is not true; it decreases, and hence the deposition becomes more and more difficult and the potential difference at the cathode increases. It is not difficult, however, to keep the value constant for a short time, and thus to find the difference of potential at the cathode.

At the same time that this takes place negative ion is separated upon the anode and the process is exactly analogous. If oxygen is the gas which separates, its concentration increases until the maximum is reached ($=P_M$) and the gas is given off into the air.

From the above it is possible to understand why a certain minimum electromotive force is required to cause a steady electrolysis. The separation takes place only when the concentration of ion around the electrodes reaches a maximum, i.e., not until the osmotic pressure exerted is great enough to overcome the solution pressure of the metal. From the case of $AgNO_3$ it would seem that this maximum of concentration need not be reached on both sides at the same time. The nature of the electrodes, so long as they are of an inert substance, has no influence except for gases, and then in the following way: The cell

$$\text{platinized Pt}+\text{H gas}-H_2SO_4-\text{O gas}+\text{platinized Pt}$$

gives an electromotive force of 1.07 volts. If 1.07 volts are passed through the cell in the opposite direction, then, we shall have equilibrium. If smaller than this, H_2O is formed at the electrodes from the gas in the electrode and the ion in the solution. If larger than 1.7, H and O are given off from the electrodes. We have here the gas-cell which gives the value 1.07 decomposing water, and reversing at 1.08. When polished platinum electrodes are used for the decomposition, however, 1.68 volts are necessary for steady electrolysis. The difference in these two values (0.6 volt) is assumed to be due to the different ion which is separated in the two cases. Water may be considered as dissociated as a dibasic acid:

$$H_2O = H^+ + OH^-$$

$$OH^- = H^+ + O^=.$$

At the value 1.68 volts the $O^=$ ion present separates, causing water to decompose for a time and then when the $O^=$ is used up the process ceases. The 1.07 volts of the gas-cell are due to this ion $O^=$, for the platinum-black gives it up to the solution in that form after having absorbed oxygen gas. When OH^- ion separates it reacts to form H_2O and O,

$$4OH^- = 2H_2O + O_2,$$

and the force necessary to do this is 1.68 volts. Where the concentration of OH^- ion is great, in bases for example, the $O^=$ ion would be present to a greater extent than in acids, and the decomposition at 1.08 should be more marked than with acids, as it is found to be. HCl has too small an amount of OH^- and $O^=$ ions to carry any amount of current, so that in strong solutions Cl separates at 1.31 volts, at which point water cannot be decomposed into hydrogen and oxygen.

If we have in a decomposition vessel one large platinized electrode and one very small one, using the latter as cathode and the large one as anode, we get a rapid decomposition of water at 1.1 volts, hydrogen being given off at the point, the oxygen being absorbed in the platinum black. We get then a reversal of the gas-battery. Using the point as anode, we get bubbles of oxygen first at 1.68 volts, hydrogen being absorbed by the large electrode. An example of the use of such a process is the Hildburgh cell (J. Am. Chem. Soc., **22**, 300, 1900), which rectifies an alternating current. If the value of the alternating current is below 1.68, current can go through when the point is the cathode and is stopped when this is the anode, as it is by the next reversal; so that we get from this a current made up of a series of impulses all in the same direction instead of the alternating current which entered. A current of large voltage can then be rectified by passage through a series of such cells. For a discussion of the passive state of a metal, which behaves similarly, see Trans. Faraday Soc., 9, 203-291, 1914.

Primary decomposition of water.—The electromotive force of decomposition of a cell giving off hydrogen and oxygen is dependent upon the concentration of the two ions H^+ and OH^-, but independent of the nature of the electrolyte. The electromotive force is the same for acids and bases so long as only H and O are separated. Since by the law of mass action the product of H^+ and OH^- ions in a solution must always be the same, it follows that for all electrolytes, since the electromotive force of the cell must be the sum of those of the two electrodes, the minimum value must be the same for all substances which give off hydrogen and oxygen. With the exception, then, of solutions of metallic salts, which are decomposed by hydrogen, and the chlorides, bromides, and iodides, which are decomposed by oxygen, the ions of water, only, are the factors in the decomposition of solutions, and those of the dissolved salt. Excluding those solutions mentioned above, then, all *solutions when electrolyzed show primary decomposition of water.* The current is conducted by all the ions in the solution. At the electrodes, however, that process takes place which requires the smallest expenditure of work, and that is the separation of hydrogen and oxygen as gases. In the case of the electrolysis of K_2SO_4 in solution, when the current is not too strong, there is no necessity for assuming that K^+ and $SO_4^=$ as ion are separated upon the electrode and then redissolved. They simply collect around the electrode, but, as the H^+ and OH^- separate more easily, these are forced out. With a stronger current, of course, it is possible to cause the separation of K^+ and $SO_4^=$, for then H^+ and OH^- ion, being present to but a small extent, cannot carry all the current, and the work of separation of the ions of the salt is smaller than that necessary to remove the very much diminished amount of OH^- and H^+. The formation and decomposition of water are reversible processes, so that there is no loss of work connected with them, while with the secondary action there would be. The H^+ and OH^- ions are formed as they are used up, i.e., more water dissociates.

All bases and acids must have the same decomposition electromotive force, for the product of the H^+ and OH^- ions is always the same. For salts we should obtain a higher value, since upon the electrode at which H separates a base is formed, and OH^- ion increases in amount, driving back that of H^+, so that the difference of potential on that electrode increases, i.e., P_M remains the same, while P decreases. On the other electrode H^+ ion collects and exerts the same decreasing effect upon the OH^- ion. The smaller the dissociation of the base and acid formed the smaller naturally this influence will be.

In the case of HCl (N/1), chlorine gas is given off steadily at a smaller electromotive force than for the oxygen acids. As the acid becomes more dilute, however, the amount of H^+ and Cl^- ions decreases, until finally there is such a large concentration of OH^- ion present, as compared with that of Cl^-, that oxygen separates the more readily. This explains the results already given for hydrochloric acid gas in different dilutions.

Electrolytic separation of metals by graded electromotive forces.—As we have seen, the salts of the different metals have different decomposition values. From this fact Freudenberg * showed how it is possible to separate metals quantitatively. It is only necessary to find two salts, i.e., one of each metal, which have decomposition values differing as much as possible. If now a certain electromotive force, lying between these limits, is passed through the cell, the metal with the lower decomposition value will separate; after that is separated, the current will cease and it is only necessary to raise the electromotive force in order to deposit the other. As the concentration of ion in the salt of the metal first separated decreases, it is necessary to raise the electromotive force slightly. This amount is small and may be readily calculated from

$$\epsilon = \frac{RT}{n_e F} \log_e \frac{P_M}{P}.$$

Thus if P decreases from 0.1 normal to 0.000001 normal (the limit by analytical means), ϵ must be increased only 0.3 volt for a monovalent element, and but half that amount for a divalent one.

An example of this is given in the table below. The decomposition voltage of $AgNO_3$ is 0.70 and that of $Pb(NO_3)_2$ is 1.52.

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* Zeit. f. phys. Chem., 12, 97, 1893.

With the two solutions present the silver will be entirely deposited by an electromotive force of less than one volt; after this is done the electromotive force may be raised to 1.52 or more and all the lead deposited.*

In this way it is possible to make separations which cannot be made by varying current strength.

The following table gives the separation value of a few ions, based on the value of H^+ taken as zero. Thus if the value of H^+ is added to that of OH^-, we have the decomposition voltage of H_2O 1.68. The values are for equivalent concentration:

$Ag^+ = -0.78$
$Cu^{++} = -0.34$
$H^+ = +0.0$
$Pb^{++} = +0.17$
$Cd^{++} = +0.38$
$Zn^{++} = +0.74$

$I^- = 0.52$
$Br^- = 0.94$
$O^= = 1.08$ (in acid)
$Cl^- = 1.31$
$OH^- = 1.68$ (in acid)
$OH^- = 0.88$ (in base)
$SO_4^= = 1.9$
$HSO_4^- = 2.6$

The values of $O^=$ and OH^- are true in the presence of a normal solution of H^+ ions. If we have H^+ and OH^- in a base, the above value of H^+ becomes 0.8 and the value of O^- and $O^=$ is decreased by 0.8.

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* The student is referred for further information to the original article.

CHAPTER X

PROBLEMS *

(*These answers were obtained by aid of a four-place table of logarithms.*)

THE GASEOUS STATE

1. An open vessel is heated to 819° C. What portion of the air which the vessel contained at 0° still remains in it? Ans. 25%.

2. An open vessel is heated until one-half of the gas that is contained at 15° is driven out of it. To what temperature was it heated? Ans. 303° C.

3. A volume of gas at 15° measures 50 cc. At what temperature would its volume become 44 cc.? Ans. 19°.6 C.

4. What is the volume of one mole of any gas at 50° and 760 millimeters pressure? What at 100° and 900 mm.? Ans. At 50°, 26.5; at 100°, 25.84 liters.

5. A volume of air in a bell jar over water measures 975 cc. The water in the jar is 68 mm. above that in the trough, and the barometer stands at 756 mm. What would be the volume of the air if it were exposed to standard pressure? The specific gravity of mercury at this temperature is 13.6. Ans. 963.4.

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* For further problems similar to these, see Prideaux, Problems in Physical Chemistry, New York, 1912; and Knox, Physico-chemical Calculations, London, 1912.

6. At 14° and 742 mm., the volume of a gas is 18 cc. What would be its volume at 0° and 760 mm.? Ans. 16.72 cc.

7. Find the molecular weight of a gas, of which 3.214 grams occupies 720.9 cc. at 300° C. and 796.3 mm. Ans. 200.

8. An enclosed volume of air changes its pressure from 1 to 0.89 atmosphere when it is increased by 450 cc. What was the original volume of the air, the temperature remaining constant throughout? Ans. 3.641 liters.

9. What is the volume of 44 grams of oxygen at 70 cm. and 35°? Ans. 37.73 liters.

10. $\frac{1}{2}$ mole of hydrogen, $\frac{1}{2}$ mole of oxygen and $\frac{1}{3}$ mole of nitrogen are mixed in a space of 10 liters at 0°. What are the partial pressures of the gases?

Ans. $p_H = p_O = 1.12$; $p_N = 0.747$ atmos.

11. What would these pressures be in 10 liters at 10°?

Ans. $p_N = p_O = 1.161$; $p_N = 0.7743$ atmos.

12. One liter of nitrogen weighs 1.2579 grams at 0° and 760 mm. Calculate the specific gas constant, r, for nitrogen.

Ans. 3009 gr. cm.

13. The specific gas constant for nitrogen is 3009, what is it for hydrogen? The atomic weight of nitrogen is 14.01, and that for hydrogen is 1.008. Ans. $r_H = 41{,}830$ gr. cm.

14. What is the weight of 100 liters of chlorine at 30° and 74 cm? Ans. 278.2 grams.

15. 0.335 gram of a gas occupies 113.8 cc. at 100° and 760 mm. What is its molecular weight? Ans. 90.07.

16. At 13.°2 and 45.9 atmospheres, the volume of a weight of CO_2 gas which occupied 1 liter at 0° and 1 atmosphere, is reduced to 0.01377 liter. Find the molecular gas constant R, in liter-atmospheres according to the equation of Van der Waals? (For data see text.) Ans. 0.08254.

17. In (16) find the theoretical value of the product $p \times v$, by aid of Van der Waals' equation, and compare it with the observed value. Ans. 0.631 calculated; 0.632 observed.

18. At 10°.4 and a certain pressure, the volume of a weight of air which at 0° and 1 atmosphere occupied 1 liter, is reduced to 0.0219 liter. Find the pressure that should have been read on the manometer, using Van der Waals' equation for the calculation. (For air we have $a = 0.0037$, $b = 0.0026$.)

Ans. $p = 46.2$ atmospheres.

19. A solid gives off a gas which is then dissociated to 41% into two products. What is the work done, in calories, gram-centimeters, and liter-atmospheres, when 1 mole of the solid goes into the gaseous state, the temperature being 55°?

Ans. 924.9 cals.; 39,210,000 gr. cm.; 37.94 lit.-atmos.

20. How much external work is done by 1000 grams of carbon dioxide when it is heated 200°, against a constant pressure? In other words, what is the difference in the amounts of work when the gas is produced from negligible volume, first at $t°$ and then at $t° + 200°$? Ans. 372.8 lit.-atmos.; 9088 cals.

21. The time necessary for the outflow of a certain volume of carbon dioxide gas through a small opening is 26.5 minutes. Under identical conditions, the time necessary for hydrogen is 5.6 minutes. Find the density (δ_H) of CO_2.

Ans. 22.44.

22. The time necessary for the outflow of another gas, under the same conditions as in (21), is 21.4 minutes. What is the molecular weight of the gas? Ans. 29.2.

23. The density of a gas referred to nitrogen as a standard (δ_N) is 2.786. The atomic weight of nitrogen is 14. What is the molecular weight of the gas? Ans. 78.

24. The density of a gas referred to gaseous mercury (molecular weight = 200) is 0.23. What is its molecular weight?

Ans. 46.

25. At 50°, under a pressure of 51.35 mm., the volume of 0.4763 gram of acetic acid vapor is 1699 cc. Show that in this state the vapor is associated.

Ans. $M_{CH_3COOH} = 60$; $M_{(CH_3COOH)_2} = 120$; $M_{calc.} = 109.9$.

26. At 50°, under a pressure of 13.4 mm. 0.6324 gram of acetic acid vapor occupies a volume of 9486 cc. Show that decreased pressure causes a decrease in the association of acetic acid vapor, i.e., reduces the molecular weight of the vapor to a more nearly normal value, as judged by the formula CH_3COOH. (See (25).) Ans. $M_{\text{calc.}} = 100.2$.

27. Hydrogen is at a partial pressure of 2.136 atmospheres in a space of 10 liters. Find the number of moles per liter present at 0°. Ans. $c_{H_2} = 0.0954$ m.p.l.

28. At 350° and 1 atmosphere, sulphuric acid is 50% dissociated according to the reaction $H_2SO_4 \rightleftarrows H_2O + SO_3$, all being gases. Starting with 55 grams of H_2SO_4 at 1 atmosphere and 350°, find the concentrations and partial pressures of H_2SO_4, SO_3 and H_2O coexisting in equilibrium at constant pressure.

Ans. $c_{H_2SO_4} = c_{H_2O} = c_{SO_3} = 0.00652$ mole per liter.
$p_{H_2SO_4} = p_{H_2O} = p_{SO_3} = 0.3334$ atmosphere.

29. Starting with 1 mole of A_2B_3 in 22.4 liters (at 0° and 760 mm.), assume the dissociation to be 23%, according to the reaction $A_2B_3 \rightleftarrows 2A + 3B$ (where A and B represent molecular weights, i.e., weights occupying like volumes under identical conditions). Find the final volume of the system under the constant pressure of 1 atmosphere. Ans. 43 liters.

30. What are the final (equilibrium) concentrations of A_2B_3, A and B in (29)?

Ans. $c_{A_2B_3} = 0.0179$; $c_A = 0.0107$; $c_B = 0.01604$ m.p.l.

31. The molecular weights in (30) are $M_{A_2B_3} = 170$, $M_A = 25$; and $M_B = 40$. Find the number of grams per liter of each constituent at equilibrium.

Ans. $w_{A_2B_3} = 3.04$; $w_A = 0.267$; $w_B = 0.642$.

32. Assume in the reaction $A_2B_3 \rightleftarrows 2A + 3B$, that we start with 17 grams of A_2B_3 ($M_{A_2B_3} = 170$) at 0° and 1 atmosphere in 2.24 liters, and find the concentrations and partial pressures, of A_2B_3, A and B, when the dissociation is 20%, and the

volume of the system and its temperature remain constant at the original values. What is the total pressure of the system?

Ans. $c_{A_2B_3}=0.036$; $c_A=0.018$; $c_B=0.027$ mole per liter.
$p_{A_2B_3}=0.8$; $p_A=0.4$; $p_B=0.6$ atmosphere.
Total pressure $=1.8$ atmospheres.

33. Starting with 0.1 mole of A_2BE_3 at 75°, knowing A_2BE_3 to dissociate to the extent of 32%, according to the reaction $A_2BE_3 \rightleftarrows 2A+B+3E$; find the concentrations and partial pressures of the constituents at equilibrium—(*a*) when the volume increases under constant, atmospheric, pressure; (*b*) when the volume remains constant at what it was for the original, undissociated, mole of A_2BE_3 at 75° and 1 atmosphere.

Ans. (*a*) $c_{A_2BE_3}=0.00916$; $c_A=0.0086$; $c_B=0.0043$; $c_E=0.0129$ mole per liter.
$p_{A_2BE_3}=0.262$; $p_A=0.246$; $p_B=0.123$; $p_E=0.369$ atmosphere.
(*b*) $c_{A_2BE_3}=0.0238$; $c_A=0.0224$; $c_B=0.0112$; $c_E=0.0336$ mole per liter.
$p_{A_2BE_3}=0.68$; $p_A=0.64$; $p_B=0.32$; $p_E=0.96$ atmosphere.

34. (*a*) Starting with 0.32 mole of A and 0.46 mole of B at 122° and constant pressure (1 atmosphere) in the gaseous reaction $2A+3B \rightleftarrows 2D+E$, we find that equilibrium is established when 0.11 mole of A is lost. Find the concentrations and partial pressures of A, B, D and E.

(*b*) Starting with the same amounts of A and B at 122°, but retaining the volume constant at what it was originally without reaction (i.e., the volume is that occupied by $0.32+0.46$ mole at 122° and 1 atmosphere) we find that 0.18 mole of A is lost. Find the concentrations and partial pressures under these conditions.

Ans. (*a*) $c_A=0.009672$; $c_B=0.01359$; $c_D=0.005066$;
$c_E=0.002533$ mole per liter.

$p_A = 0.3134$; $p_B = 0.4402$; $p_D = 0.1642$; $p_E = 0.0821$ atmosphere.

(*b*) $c_A = 0.005539$; $c_B = 0.007518$; $c_D = 0.007122$; $c_E = 0.003561$ mole per liter.

$p_A = 0.1795$; $p_B = 0.2435$; $p_D = 0.2308$; $p_E = 0.1154$ atmosphere.

35. At 100° the dissociation pressure of $NaHCO_3$, breaking down according to the reaction $NaHCO_3 \rightleftarrows \frac{1}{2}Na_2CO_3 + \frac{1}{2}H_2O + \frac{1}{2}CO_2$ (where the H_2O and CO_2 are gaseous, and the others are solid) is 310 mm. Find the concentrations and partial pressures of H_2O and CO_2.

Ans. $c_{H_2O} = c_{CO_2} = 0.00667$ mole per liter.
$p_{H_2O} = p_{CO_2} = 0.204$ atmosphere.

36. In the reaction $A_2B \rightleftarrows 2A + B$, A_2B is a solid which practically does not exist as a gas, and A and B are gases. At 100°, the dissociation pressure of A_2B (i.e., of the gases produced from it) is 2 atmospheres. Find the partial pressures and concentrations of A and B.

Ans. $p_{A_2B} = 0$; $p_A = 4/3$; $p_B = 2/3$ atmosphere.
$c_{A_2B} = 0$; $c_A = 0.0436$; $c_B = 0.0218$ mole per liter.

37. When phosphorus pentachloride is heated it gasifies and dissociates into the trichloride and chlorine $PCl_5 \rightleftarrows PCl_3 + Cl_2$. The molecular weight of PCl_5 is 208.34. At 182°, the density, referred to hydrogen as a unit (i.e., δ_H) is 73.5, while at 230° it is 62. Find the degree of dissociation at 182°. At 230°.

Ans. $\alpha_{182°} = 0.417$; $\alpha_{230°} = 0.68$.

38. Sulphur, S_8, dissociates under certain conditions into the form S_2. If this dissociation were complete, what would be the density of the system referred to chlorine (atomic weight $= 35.46$)?

Ans. $\delta_{Cl} = 0.9014$.

39. How many atomic weights are there in the molecular weight of argon, its specific heat for constant volume being 0.075? According to density determinations, the molecular weight of argon is 40.

Ans. 1.

40. The time necessary for the outflow of a certain volume of a diatomic gas through a small opening is 22.3 minutes. Under identical conditions the time for hydrogen is 5.6 minutes. What is the specific heat of the gas at constant volume?

Ans. 0.1524.

41. The specific heat for constant pressure, s_p, of benzene ($M=78$) is 0.295, what is its specific heat at constant volume, s_v?

Ans. 0.269.

42. The specific heat s_p, of carbon dioxide gas is 0.2036; what is the calculated value of the ratio of specific heats for CO_2?

Ans. $\gamma=\frac{s_p}{s_v}=1.29$.

43. Find the specific heat at constant volume of hydrogen gas at 27°. For data, see text.

Ans. $s_p=2.4$.

44. Air, for which $\gamma=1.4$, compressed to a pressure equal to 50 atmospheres, is allowed to expand *rapidly* to double its initial volume. What is the temperature of the gas produced by the expansion, assuming the original temperature to have been 0°?

Ans. $-66°.1$ C.

45. Two gases, $\gamma_1=1.4$ and $\gamma_2=1.22$, are compressed *rapidly*, each to one-tenth of its original volume. What temperatures are produced in the gases, if 0° were the original ones?

Ans. $t_1=412.°8$; $t_2=180°.1$ C.

46. A mixture of hydrogen and oxygen gases is compressed *rapidly* from the volume of 40.1 cc. to 3.04 cc., the temperature rising from 20° to 549° C. What is the value of γ for the gaseous mixture?

Ans. 1.4.

47. A mixture of gases is compressed *rapidly* from the pressure 1.74 to 64.3 atmospheres, the intitial temperature being 20°, and $\gamma=\frac{s_p}{s_v}=1.4$. Find the final temperature of the gaseous system.

Ans. 549°.6 C.

48. The volume of a mixture of gases is changed *rapidly*

from 227.8 cc. to 18.85 cc., $\gamma = 1.4$, and the initial pressure was 1.25 atmospheres. What is the final pressure?

Ans. 40.9 atmospheres.

THE LIQUID STATE

49. The Van der Waals' constants for benzene are $a = 0.03727$, and $b = 0.005369$. Calculate the critical temperature and pressure of benzene.

Ans. $t = 288.5$; obs. $t = 288^\circ.5$;
$p_c = 47.87$; obs. $p_c = 47.91$ atmospheres.

50. For carbon disulphide, b of Van der Waals' equation has a value of 0.003225. Find the critical volume of CS_2.

Ans. 0.00968; obs. value, 0.0096.

51. Calculate the critical temperature of a mixture containing 63.96 parts by weight of ether and 36.04 of benzene. The critical temperatures of the pure liquids are 193.°5 and 288°.5, respectively. Ans. 227°.8; obs. 231°.

52. A volume of 50 liters of air in passing through a liquid at 22° causes the evaporation of 5 grams. What is the vapor-pressure of the liquid ($M = 100$) in millimeters of mercury?

Ans. 18.4 mm.

53. The vapor-pressure of a liquid is 44 mm. at 20°, its molecular weight as a gas being 46. How many grams will evaporate when 100 liters of air are bubbled through it? Ans. 11.09.

54. Normal hexane ($M = 86.1$) has a molecular volume as a gas at 60° equal to 34,500 cc., while as a liquid the same weight occupies 137.96 cc. What is the latent heat of evaporation of hexane per gram? Ans. 85.4 cals.

55. For carbon dioxide at 0° the density (d) in the gaseous state is 0.099, and in the liquid state 0.905. What is the latent heat of evaporation of CO_2 per gram?

Ans. 54.9; obs. 57.48 cals.

56. The latent heat of evaporation of chloroform at 61°, its boiling-point under atmospheric pressure, is 58.49 cals.

The molecular weight as a gas is 119.1. What is its formula in the liquid state? Ans. $M = 118$.

57. The latent heat of methyl alcohol at its boiling-point, 66,° is 267.48 cals., the molecular weight as a gas being 32. Show that methyl alcohol is an abnormal, or associated, liquid.

58. The heat of evaporation of ether at 34°.5 is 88.39 cals. per gram. Find the change in boiling-point due to a change in pressure from 760 to 634.8 mm. Ans. $-4°.76$.

59. s_v for gaseous benzene (C_6H_6) at 50° is 0.269 (see 41); for liquid benzene at the same temperature the specific heat is 0.4502. What is the change in the heat of evaporation per degree of benzene around 50°? Ans. -0.1557 cal. per degree.

60. 1 gram of a liquid as a gas at 100° and 760 mm. occupies the volume of 413.5 cc. and $\frac{s_p}{s_v} = 1.097$. The heat of evaporation at 15°.5 is 89.25, and at 34°.83 is 84.5 cals. Find the specific heat of the liquid. At what temperature should this value hold, if the specific heat varies with the temperature?

Ans. 0.5514; obs. 0.545; $t = 25°.16$.

61. The latent heat of evaporation of liquid ammonia (NH_3), at its boiling-point ($-33°.5$) under atmospheric pressure, is 341 gram calories per gram. Is liquid ammonia associated or non-associated?

62. The boiling-point, under atmospheric pressure, of hexane, (C_6H_{14}), is 69°. What is its latent heat of evaporation, assuming that it is non-associated? Ans. 82.5; obs. 82.9 cals.

63. The boiling-point, under atmospheric pressure, of *p*-nitrotoluene, ($C_7H_7NO_2$), is 237°.7; while its latent heat of evaporation is 84 cals. What is its molecular weight in the liquid state? Ans. 137.5.

64. Find the heat of evaporation of ethyl formate. $\frac{\Delta p}{\Delta t} = 27$ mm., the boiling-point at 760 mm. is 54.3, and its molecular weight is 74. Ans. 102.8 cals. per gram.

65. Find $\frac{\Delta p}{\Delta T}$ for the liquid. Its heat of evaporation is 77 cals. per gram, the density in the gaseous state (d) is 0.0033, and its density as a liquid is 0.7958, both at the boiling-point, under atmospheric pressure, 99°. Ans. 21.37 mm.

66. What is the heat of evaporation of ether at 80°, i.e. assuming the external pressure is so increased as to raise the boiling-point from 35 to 80°? The specific heat of ether as a liquid at 80° is 0.690; its molecular weight as a gas is 74, and the heat of evaporation at 35° is 88.39 cals. per gram. (For further data see text.) Ans. 77.13 cals. per gram.

67. Find $\frac{\Delta T}{\Delta p}$ for ether at 80° in (66); the vapor pressure at 80° is 299.14 cm. Ans. 0°.0146 per mm.

68. What is the change in the vapor-pressure per degree of ether around 80°? (See (67).) Ans. 68.5 mm. per degree.

69. What change in the external pressure is necessary to increase the boiling-point of ether from 35° to 80° in (66)?
Ans. 4.06 atmos. increase.

70. The boiling-point of the non-associated liquid methyl propionate, is 79°.7 at atmospheric pressure. Find the change in vapor-pressure per degree around this point.
Ans. 24.05 mm./degrees; obs. 25.0 mm./degrees.

71. Find the boiling-point of propyl acetate, a non-associated liquid, at 723.6 mm. Under atmospheric pressure, it boils at 101.°6. Ans. 100°; obs. 100°.

72. Find the vapor-pressure of the associated liquid, water, at 99°, the boiling-point under atmospheric pressure, is 100°.
Ans. 732.7 mm.; obs. 733 mm.

73. Find the boiling-point of water under a pressure of 775 mm. (See (72).) Ans. 100°.55; obs. 100°.55.

74. (a) Find the boiling-point, under a pressure of 700 mm., of the associated liquid, ethyl alcohol, which boils at 78° under atmospheric pressure. Ans. 75°.9; obs. 76°.1.

(*b*) Find the vapor-pressure of ethyl alcohol at 74°.4.
Ans. 655.4 mm.; obs. 650. mm.

75. The refractive index of liquid nitrogen is 1.2062; of liquid air it is 1.2053. Find the refractive index of liquid oxygen. Air is composed of 23.01% of oxygen and 76.99% nitrogen, both by weight, and the densities are $d_O = 1.124$; $d_{air} = 0.9673$; $d_N = 0.885$. Ans. 1.16.

76. What is the surface tension of benzene in dynes per centimeter? The height to which it ascends at 46° in a capillary tube of 0.1843 mm. bore-radius is 32.12 mm.; and its density is 0.85. Ans. 24.66 dynes per cm.

77. Find the height to which carbon disulphide will ascend in a capillary tube of 0.3416 mm. bore, the surface tension being 29.41 dynes per centimeter, and the density 1.224.
Ans. 2.87 cm.

78. Find the molecular weight of benzene as a liquid from the Ramsay and Shields relationship. The surface tension at 46° is 24.71 dynes, its critical temperature is 288°.5, $k = 2.12$, and the density is 0.85. Ans. 77.6; theoretical 78.

79. Find the molecular weight as a liquid of carbon disulphide, by the Ramsay and Shields formula. Its surface tension at 46°, as found by Ramsay and Shields, is 29.41 dynes, its density is 1.224, and its critical temperature is 280°.3.
Ans. 81.7; theoretical 76.

80. At 14.°8, acetyl chloride ($M = 78.5$) ascends to a height 32.8 mm. in a capillary tube of 0.1425 mm., its density being 1.124. At 46.°2 in the same tube, the height of ascension is 28.5 mm. and the density is 1.064. Find the critical temperature by the Ramsay and Shields formula, using $g = 981.1$.
Ans. 234.°6.

81. Find the factor of association of formic acid, (CH_2O_2), between 16°.8 and 46°.4, by the Ramsay and Shields method. At 16°.8, $h = 4.442$ cm., $r = 0.0285$ cm.; $d = 1.207$, $g = 981.1$; at 46°.4, $h = 4.205$, $d = 1.170$. Ans. 3.61.

82. Show the molecular weight, as a liquid, of dipropyl ketone, $(C_3H_7)_2CO$, by the Morgan definition of normal molecular weight, to be normal. At 10°, $\gamma = 25.802$, $d = 0.8258$; at 30°, $\gamma = 23.883$, $d = 0.8105$; at 40°, $\gamma = 22.968$, $d = 0.8029$; and at 60°, $\gamma = 21.228$, $d = 0.7877$.

83. Is amyl formate $(C_6H_{12}O_2)$ associated or non-associated according to the Morgan definition? At 0°, $\gamma = 25.537$, $d = 0.9063$; at 60°, $\gamma = 20.405$, $d = 0.8422$. Ans. Associated.

THE SOLID STATE

84. The specific heat of metallic nickel is 0.1092, show that 58.68, rather than some multiple or submultiple of that, should be chosen as the atomic weight of nickel.

85. The specific heat of metallic iron is 0.112. Show that 55.84 should be the atomic weight of iron.

86. The specific gravity of solid phenol is 1.072, while in the liquid state it is 1.0561. Knowing, further, that the latent heat of fusion is 24.93 calories per gram at the melting-point, 34°, find the change in the melting-point due to a change in pressure. Ans. $\frac{\Delta T}{\Delta p} = +0^\circ.0042$ per atmosphere.

87. The heats of solution in water of 1 gram of solid, and of 1 gram of liquid, acetic acid at the melting-point 16°.6, are -40.8 and $+5.58$ cals. respectively. What is the change in melting-point per degree around the melting-point. The excess of specific volume of the liquid phase, over that of the solid, is 0.1595 cc. Ans. 0.0243 degree/atmos.

88. The specific heat of solid acetic acid is 0.4599 from 10° to 15°, while that of the liquid is 0.5026. Find the heat of fusion at 50° from that at 5.6, which is 44.34 cals.

Ans. 46.24 cals. per gram.

89. Naphthalene in the solid state has a specific heat of 0.356, while that of the liquid state is 0.396, and the heat of

fusion is 37.5 cals. per gram, all at 80°. What is the heat of fusion at 30°? Ans. 33.5 cals. per gram.

90. Assuming the data in (89), find *the fraction* of liquid naphthalene that would separate as a solid at 80°, as the result of an overcooling of 10°. Ans. 11.2%.

91. The heat of fusion of ice is 80 calories, while the heat of evaporation of water is 597, both at 0°. What is the heat of sublimation of ice at 0°? Ans. 677 cals. per gram.

92. How could the heat of sublimation of ice at 0° (91) be calculated from the following data? The specific volume of water vapor at 0° is 204,680 cc. (for this is the volume of 1 gram of water vapor, at the vapor-pressure 4.62 mm.), that of ice is 1.09 cc., and the change in the vapor-pressure per degree for ice around 0° is 0.364 mm.

Ans. 652.6 cals. per gram.

93. The specific gravity of water at 0° is 1, and the heat of solidification is 80 cals. per gram. Find the change in the freezing-point of water which results from an increase in pressure of 2 atmospheres. (For data, see (92).)

Ans. $-0^\circ.01498$.

94. The specific heat in the liquid state of a liquid is 0.43, that for the solid phase is 0.352. An overcooling of $17.^\circ8$ causes one-quarter of the liquid to separate as a solid. What is the latent heat of fusion of the liquid at its freezing-point? What at 10° below its freezing-point?

Ans. 30.6 and 29.84 cals. per gram.

95. The specific heat of phosphorus in the liquid state, at 44°, is 0.204, while its latent heat of fusion is 5 cals. At $39^\circ.5$ the latent heat of fusion is 4.86 cals. per gram. Calculate the specific heat in the solid state. Ans. 0.173.

96. At 29°, the latent heat of fusion of $CaCl_2 \cdot 6H_2O$ is 40.7 cals., and at -160 is 0. Find the specific heat in the liquid state, knowing that in the solid state it is 0.345.

Ans. 0.560.

97. The specific heat of liquid $CaCl_2 \cdot 6H_2O$ from (96) is, 0.560, the latent heat of solidification at the same, fusion, temperature (29°), is 40.7 cals. per gram. How many grams of liquid are separated as solid by overcooling 75 grams of liquid $CaCl_2 \cdot 6H_2O$, through 2°.34? Ans. 2.415 grams.

SOLUTIONS

98. 1 liter of water absorbs a liter of carbon dioxide gas at 0° and 1 atmosphere pressure. How many grams of CO_2 gas must be contained in a bottle of carbonic water holding 350 cc. of the solution, under a pressure of 5 atmospheres?

Ans. 3.44 grams.

99. Air is composed of 20.9 volumes of oxygen and 79.1 of nitrogen. At 15°, water absorbs 0.0299 volumes of oxygen and 0.1048 of nitrogen, the volumes being measured at 0° and 1 atmosphere pressure. What is the composition of the air absorbed in water?

Ans. 34.8% by volume of O_2, and 65.2% of N_2.
37.88% by weight of O_2, and 62.12% of N_2.

100. What would be the composition dissolved, if that dissolved in (99) were expelled and re-dissolved in fresh water?

Ans. 51.9% of O_2, and 48.1% of N_2 by volume.

101. For systems containing the immiscible liquids, water and chlorbenzene, we find the following:

t	C_6H_5Cl	H_2O	Total
—	p_1	p_2	p_1+p_2
90°	208.35 mm.	524.45	733.8
91	215.8	545.8	761.6
92	223.45	566.75	790.2

Find the percentage by weight of C_6H_5Cl distilling.

Ans. average = 71.2%; obs. = 71.4%.

102. The molecular weight of water, as a gas, is 18, and that of a certain liquid is 121. The vapor-pressure at 99° (the

boiling-point of the immiscible liquid system) of pure water is 733 mm., and that of the liquid is 27 mm. How much of the liquid is contained in the distillate?

Ans. 20% of the total weight in grams.

103. What is the osmotic pressure of a solution of glucose ($M=180$), containing 1 gram in 100 cc. of water at 0°?

Ans. 94.6 cm.; obs. = 94.0.

104. The osmotic pressure of a solution of cane-sugar at 0° is 49.3 cm. What weight of sugar ($M=342$) is contained on 100 cc. of water? Ans. 0.99 gram; obs. 1.00.

105. The osmotic pressure of a sugar solution at 32° is 54.4 mm. What is it at 14°.2? Ans. 51.2 mm.

106. The osmotic pressure of a solution containing 10 grams of sugar to a certain volume of water is 200 mm. What is it for the same volume containing 13.5 grams?

Ans. 270 mm.

107. 1 mole of sugar (342 grams) is dissolved in 1 liter of water. Find the osmotic pressure at 22°.45.

Ans. 24.2 atmos.; obs. 24.5.

108. The addition of 10.442 grams of aniline to 100 grams of ether produces a solution with a vapor pressure of 210.8 mm. Ether alone ($M=74$) has a vapor-pressure, at the same temperature, of 229.6. Find the molecular weight of aniline in solution in ether. Ans. 86.6.

109. Find the osmotic pressure in atmospheres at 0°, of the aniline dissolved in ether in (108). The density of ether is 0.737.

Ans. 19.82 atmos.

110. The osmotic pressure of a substance in water solution is 1000 cms. Find the vapor-pressure of the solution; that of pure water, at the same temperature, is 4.57 mm.

Ans. 4.52 mm.

111. What is the work in gram-centimeter, and calories necessary to separate by isothermal osmotic work the amount of solvent which contained 200 grams of a substance ($M=60$)

from a very large amount of the solution at 20°? To every liter of solvent there are 10 grams of dissolved substance.

Ans. 1953 cals.; 82,790,000 gr.-cms.

112. 64.74 grams of propylene bromide ($M = 222$) are mixed with 145.93 grams of ethylene bromide ($M = 206$) at 85°.05; the vapor-pressure of the former at this temperature is 127.2 mm., while that of the latter is 172.6. What are the partial vapor-pressures of each in the mixture? What is the composition of the distillate? What is the total vapor-pressure of the mixture? All on the assumption that no chemical reaction takes place between the constituents.

Ans. *v. p.* (ethyl. br.) = 122.3 mm.; obs. 121.4,
v. p. (prop. br.) = 37.1 mm.; obs. 37.3.
Total vapor pressure = 159.4; obs. 158.7.

In each 100 grams of distillate there are 24.6 grams of propylene bromide and 75.4 grams of ethylene bromide. The observed values being 24.91 and 75.1.

113. The increase in the boiling-point of 54.65 grams of carbon disulphide by the addition of 1.4475 grams of phosphorus is 0°.486. What is the molecular weight of phosphorus dissolved in carbon disulphide? $K_{b.p.}$ for CS_2 is 2.37.

Ans. 129.2.

What is the formula of phosphorus in this condition? Its atomic weight is 31.

114. Calculate the increase in the boiling-point ($K_{b.p.}$) of ether when to 1000 grams, we add 1 mole of any substance. The boiling-point under atmospheric pressure of ether is 34°.97 and the latent heat of evaporation is 88.39 cals. per gram.

Ans. 2°.15.

115. The boiling-point constant ($K_{b.p.}$) of water, as caused by the addition of 1 mole of any substance to 1000 grams, is 0°.52. Find the heat of evaporation of water, at its boiling-point, 100°. Ans. 535.1 cals. per gram.

116. At 40°, the change of vapor-pressure per degree of

benzene ($M=78$) is 0.881 mm., for a mean pressure of 22.42 cms. What is the boiling-point constant ($K_{b.p.}$) of benzene, under this reduced pressure? Ans. 1°.985.

117. The addition of 10 grams of a substance to 100 grams of solvent increases its boiling-point by 0°.87. The molecular weight of the substance, in the solution, is 60. Find the boiling-point constant ($K_{b.p.}$). Ans. 0°.522.

118. The increase of the boiling-point of an aqueous solution is 0°.21. What is the osmotic pressure of the substance in solution at 100° ($d_{H_2O}=1$)? $K_{b.p.}=0°.52$. Ans. 11.85 atmospheres.

119. From (118) find the vapor-pressure of the solution at 100°, that of the pure solvent being 760 mm. Ans. 754.6 mm.

120. The addition of 0.284 gram of the oxime, $(CH_3)_2CNOH$, causes a decrease of 0°.155 in the freezing-point of 100 grams of glacial acetic acid. $K_{b.p.}$ for acetic acid is 3°.88. Find the molecular weight of the oxime in acetic acid solution.

Ans. 71.

121. The addition of 2 moles of a substance to 2000 grams of water causes a depression of the freezing-point of 2°.1, when the overcooling produced in the freezing is 2.°21. What is the strength of the solution whose freezing-point is observed? (For data, see text.)

Ans. 1.028 moles per 1000 grams of water.

122. Find the freezing-point depression of the solution itself in (121). Ans. 2°.042.

123. Find the heat of fusion of nitrobenzene; its melting-point is 5°.3, the freezing-point constant ($K_{b.p.}$) is 7.05.

Ans. 21.97 cals. per gram.

124. The specific heat of liquid nitrobenzene is 0.3524, its heat of fusion (123) is 21.97 cals. The observed depression caused by the addition of 10 grams of a substance to 72.5 grams of nitrobenzene is 1°.21, when the overcooling is 1°. What is the strength of the solution whose freezing-point is observed?

Ans. 140.2 grams of substance per 1000 grams.

125. Find the osmotic pressure at 46° of a solution containing 1.4475 grams of phosphorus in 54.65 grams of carbon disulphide. The molecular weight of phosphorus in this solution is 4×31, and the density of carbon disulphide at this temperature is 1.224. Ans. 6.84 atmos.

126. Find the vapor-pressure in (125) of the carbon disulphide solution of phosphorus at 0°; the vapor-pressure of carbon disulphide at 0° is 127.91 mm. Ans. 125.9 mm.

127. Find the osmotic pressure of a solution of 0.284 gram of the oxime, $(CH_3)_2CNOH$, in 100 grams of glacial acetic acid at 17°. The density of acetic acid, at this temperature, is 1.056. Ans. 0.978 atmos.

128. What is the relation between the osmotic pressures of a solution containing 0.01 mole of substance in 1000 grams of water, on the one hand, and one made up of the same weight of substance in 1000 grams of ether ($d=0.7370$), on the other, assuming the same molecular weight of the substance in both solvents? Ans. $P_e=0.737\ P_w$.

129. Find the vapor-pressure of the solution containing 0.284 gram of the oxime, $(CH_3)_2CNOH$, in 100 grams of glacial acetic acid at 40°, the vapor-pressure of glacial acetic acid, at that temperature, being 34.77 mm. Ans. 34.69 mm.

130. Find the molecular weight of 0.4212 gram of KCl in solution in 60 grams of molten $CaCl_2 \cdot 6H_2O$. The observed depression of the freezing-point is from 29°.48 to 29°.057; the heat of fusion of solid $CaCl_2 \cdot 6H_2O$ at is melting-point being 40.7 cals. per gram. Ans. 74.7.

131. $K_{f.p.}$ for molten $LiNO_3 \cdot 3H_2O$, at its freezing-point 29°.88, is 2°.6. What is the latent heat of fusion of solid $LiNO_3 \cdot 3H_2O_2$? Ans. 70.6 cals. per gram.

132. A solution containing a 0.1 of a mole of acetic acid in 1000 grams of water shows a depression of the freezing-point of 0°.1927. Find the degree of ionization of acetic acid. $CH_3COOH \rightleftarrows CH_3COO^- + H^+$. $K_{f.p.}=1°.86$. Ans. $\alpha=0.036$.

133. A solution containing 0.15 mole of succinic acid in 1000 grams of water shows a depression of the freezing-point of 0°.2864. Find the degree of ionization of the acid, which ionizes into 1 mole of hydrogen ion and 1 mole of the negative ion, just as acetic acid does in (132). Ans. $\alpha = 0.027$.

134. A substance of which 0.1 mole is dissolved in 1000 grams of water ionized to 32.4% into 3 ions (i.e., is of the type $BaCl_2 \rightleftarrows Ba^{++} + 2Cl^-$). Find the freezing-point ($K_{f.p.} = 1.86$); the boiling-point ($K_{b.p.} = 0.52$); the osmotic pressure at 28°; and the vapor-pressure at 0° (the vapor-pressure of water at 0° is 4.57 mm.) of the solution. We assume here, for simplicity, which is not true experimentally, that the ionization remains constant in extent at all the temperatures,

Ans. F.p. = −0°.3065; B.p. = 100°.086.

Osmotic pressure = 4.07 atmos.; vap.press. = 4.556 mm.

135. From the "observed" values for the ionization of potassium chloride, page 334, calculate by Bodländer's method the ionization of a 0.5 molar solution of $BaCl_2$, which ionizes into $Ba^{++} + 2Cl^-$. Ans. $\alpha = 0.56$.

136. Calculate as in (135) the degree of ionization of a 0.05 molar solution of $MgSO_4$ ($MgSO_4 \rightleftarrows Mg^{++} + SO_4^{=}$).

Ans. $\alpha = 0.53$.

137. Find α (by Noyes' method) for the solution in (136) at 18°, knowing that α for 0.05 molar K_2SO_4 ($= 2K^+ + SO_4^{=}$) is equal to 0.69. Ans. $\alpha = 0.38$; obs. 0.36.

138. The freezing-point of 0.25 mole of KCN in 1000 grams of water is −0°.86. The freezing-point of the same solution, after the addition of 0.25 mole of AgCN to it, is −0°.83. The solution of AgCN in KCN takes place according to the equation,

$$mCN^- + AgCN = AgCN(CN)m.$$

What is the value of m? $K_{f.p.} = 1.86$. Ans. m = 1.036.

THERMOCHEMISTRY

139. Find the heat of decomposition of hydrogen peroxide into water and oxygen.

$$SnCl_2 \cdot 2HCl \cdot Aq + O = SnCl_4 \cdot Aq + H_2O + 657 \text{ Kal.}$$

$$SnCl_2 \cdot 2HCl \cdot Aq + H_2O_2 \cdot Ag = SnCl_4 \cdot Aq + 2H_2O + 888 \text{ Kal.}$$

Ans. $H_2O_2 = H_2O + O + 231$ Kal.

140. The heat of combustion of ammonia in oxygen at constant volume and 18° is

$$2NH_3 + 3O \rightleftarrows 3H_2O + N_2 + 1812 \text{ Kal.}$$

Knowing also that

$$H_2 + O = H_2O + 674.84 \text{ Kal.,}$$

under the same conditions, find the heat of formation of ammonia from its elements.

Ans. $N + 3H = NH_3 + 106.26$ Kal. $\left\{\begin{array}{l}\text{constant}\\ \text{volume,}\\ \text{and } 18^\circ.\end{array}\right.$

141. How does the heat of combustion of hydrogen in oxygen to form 18 grams of liquid water at constant volume vary with the temperature? The heat capacity of 72 grams of water is 0.72 Kal., and that of 4 grams of hydrogen plus 32 grams of oxygen is 0.2056 Kal. Ans. -0.0772 Kal. per degree.

142. $CH_4 + 2O_2 = CO_2 + 2H_2O + 2119$ Kal; $C + O_2 = CO_2 + 970$ Kal, and $H_2 + O = H_2O + 683.57$ Kal, all at constant pressure and 18°. Find heat of formation of CH_4 from its element at constant volume and 18°.

Ans. $C + 2H_2 = CH_4 + 218.2$ Kal.

143. Find the heat of the reaction $H_2+2\mathrm{I}=2\mathrm{HI}$:

$$2\mathrm{KIAq}+Cl_2=2\mathrm{KClAq}+2\mathrm{I}+524\ \text{Kal.}$$

$$\mathrm{HIAq}+\mathrm{KOHAq}=\mathrm{KIAq}+\mathrm{H_2O}+137\ \text{Kal.}$$

$$\mathrm{HClAq}+\mathrm{KOHAq}=\mathrm{KClAq}+\mathrm{H_2O}+137\ \text{Kal.}$$

$$2\mathrm{HI}+\mathrm{Aq}=2\mathrm{HIAq}+384\ \text{Kal.}$$

$$2HCl+\mathrm{Aq}=2\mathrm{HClAq}+346\ \text{Kal.}$$

and

$$H_2+Cl_2=2HCl+440\ \text{Kal.}$$

Ans. $H_2+2\mathrm{I}=2\mathrm{HI}-122$ Kal.

144. $\mathrm{K}+\mathrm{Aq}=\mathrm{KOHAq}+H+481$ Kal.

and

$$H_2+O=\mathrm{H_2O}+683.57\ \text{Kal.}$$

Find the heat of formation from the elements of KOHAq.

Ans. $\mathrm{K}+H+O+\mathrm{Aq}=\mathrm{KOHAq}+1164.57$ Kal.

145. $\mathrm{Zn}+\mathrm{HClAq}=\mathrm{ZnCl_2Aq}+H_2+342$ Kal. at constant pressure, and 20°. What is the heat developed at constant volume at 20°. Ans. 347.9 Kal.

146. The following reactions,

$$C_6H_6+15O=6CO_2+3H_2O+y\ \text{Kal.}$$

and

$$\mathrm{C_6H_6}+15O=6CO_2+3\mathrm{H_2O}+x\ \text{Kal.}$$

take place at 27° and constant pressure. Find the values at constant volume and 27°. It is to be especially remembered here that gases are designated by italics and solids and liquids, or substances in solution, are in ordinary type, since the volume (and the change of volume) of the system is dependent upon the gaseous constituents.

147. Find the heat of formation from the elements of phos-

phorus trichloride, $P+3Cl=PCl_3$. The following reactions have been observed:

$$PCl_3+3H_2O+Aq=P(OH)_3Aq+3HClAq+651 \text{ Kal.}$$
$$H_2+Cl_2+Aq=2HClAq+786 \text{ Kal.}$$
$$2P+3O+3H_2O+Aq=2P(OH)_3Aq+2504 \text{ Kal.}$$
$$H_2+O=H_2O+683.57 \text{ Kal.}$$

Ans. $P+3Cl=PCl_3+754.6$ Kal.

148. Find the heat of formation from the elements of $H_2S_4O_6$ Aq. The following reactions have been measured:

$$H_2+2I+Aq=2HIAq+263 \text{ Kal.}$$
$$2Na_2S_2O_3Aq+2I=Na_2S_4O_6Aq+2NaIAq+80 \text{ Kal.}$$
$$2NaOHAq+2HIAq=2NaIAq+2H_2O+274 \text{ Kal.}$$
$$2H_2+O_2=2H_2O+1368 \text{ Kal.}$$
$$4NaOHAq+2H_2S_2O_3Aq=2Na_2S_2O_3Aq+4H_2O+594 \text{ Kal.}$$
$$2NaOHAq+H_2S_4O_6Aq=Na_2S_4O_6Aq+4H_2O+271 \text{ Kal.}$$
$$4S+2O_2+Aq=2H_2S_2O_3Aq+1378 \text{ Kal.}$$

Ans. $H_2+4S+3O_2+Aq=H_2S_4O_6Aq+2612$ Kal.

149. Find the heat of formation from the elements of $HClO_3Aq$.

$$2KClO_3=2KCl+3O_2+194 \text{ Kal.}$$
$$KClO_3+Aq=KClO_3Aq-100 \text{ Kal.}$$
$$H_2O+KClO_3Aq=KOHAq+HClO_3Aq-138 \text{ Kal.}$$
$$KCl+Aq=KClAq-44 \text{ Kal.}$$
$$2H_2O+2KClAq=2KOHAq+2HClAq-276 \text{ Kal.}$$
$$2H_2+2Cl_2+Aq=4HClAq+1572 \text{ Kal.}$$

Ans. $H+Cl+3O+Aq=HClO_3Aq+240$ Kal.

150. Find the heat of formation from the elements of HFAq.

$$\mathrm{K_2SO_3Aq}+2\mathrm{KOHAq}+2F=\mathrm{K_2SO_4Aq}+2\mathrm{KFAq}+\mathrm{H_2O}+1280\ \mathrm{Kal}$$
$$2\mathrm{KOHAq}+2\mathrm{HFAq}=2\mathrm{KFAq}+2\mathrm{H_2O}+326\ \mathrm{Kal.}$$
$$2\mathrm{KOHAq}+\mathrm{H_2SO_3Aq}=\mathrm{K_2SO_3Aq}+2\mathrm{H_2O}+290\ \mathrm{Kal.}$$
$$\mathrm{H_2SO_3Aq}+O=\mathrm{H_2SO_4Aq}+637\ \mathrm{Kal.}$$
$$2\mathrm{KOHAq}+\mathrm{H_2SO_4Aq}=\mathrm{K_2SO_4Aq}+2\mathrm{H_2O}+314\ \mathrm{Kal.}$$
$$2H_2+O_2=2\mathrm{H_2O}+1368\ \mathrm{Kal.}$$

Ans. $H_2+F_2+\mathrm{Aq}=2HF+2\times488.5$ Kal.

151. What is the difference in energy between 18 grams of water at 100° and 18 grams of water vapor at the same temperature? Between the same weight of ice and water at 0°? The latent heat of evaporation is 536.4, and of fusion is 80 cals. per gram. Ans. 9656 and 1440 cals.

152. Find the heat of formation from the elements of gaseous hydrobromic acid.

$$\mathrm{SO_2Aq}+O=\mathrm{SO_3Aq}+63{,}700\ \mathrm{cals.}$$
$$2\mathrm{Br}+\mathrm{SO_2Aq}+\mathrm{H_2O}=2\mathrm{HBrAq}+\mathrm{SO_3Aq}+54{,}000\ \mathrm{cals.}$$
$$H_2+O=\mathrm{H_2O}+68{,}400\ \mathrm{cals.}$$

and

$$HBr+\mathrm{Aq}=\mathrm{HBrAq}+20{,}000\ \mathrm{cals.}$$

Ans. $H+\mathrm{Br}=HBr+9350$ cals.

153. Find the heat of formation, and the heat of formation in infinite dilution, of ammonia.

$$2NH_3+3O=N_2+3\mathrm{H_2O}+181{,}200\ \mathrm{cals.}$$
$$3H_2+3O=3\mathrm{H_2O}+3\times68{,}400\ \mathrm{cals.},$$

both at constant pressure, and

$$NH_3+\mathrm{Aq}=\mathrm{NH_3Aq}+8400\ \mathrm{cals.}$$

Ans. $N+3H=\mathrm{NH_3}+12{,}000$ cals. at constant pressure.
$N+3H+\mathrm{Aq}=\mathrm{NH_3Aq}+20{,}400$ cals.

154. $NaOH+50H_2O$ has a heat capacity equal to 885 cals., and SO_3+100H_2O that of 1797 cals., i.e., these are the amounts of heat necessary to raise the temperatures 1° respectively. At 9°.16, when mixed, these systems evolve 32,060 cals., while at 24°.42 they evolve 31,650 cals. What is the specific heat of a solution $Na_2SO_4+200H_2O$? The atomic weights are $Na=23$, $S=32$, and $O=16$.

Ans. 0.9603 cal. per gram.

155. At constant pressure and 18°

$$N_2O_4+H_2O+Aq=HONOAq+HONO_2Aq+155 \text{ Kal.}$$

$$H_2+2O_2+N_2+Aq=2HONOAq+616 \text{ Kal.}$$

$$H_2+3O_2+N_2+Aq=2HONO_2Aq+984 \text{ Kal.}$$

$$2H_2+O_2=2H_2O+1368 \text{ Kal.}$$

Find the heat x in

$$N_2O_4=N_2+2O_2+x \text{ Kal.},$$

at constant volume and 8°. The specific heats per gram are 0.2438 for N, 0.2175 for O, and 0.65 for N_2O_4, *all in calories at 18° and constant pressure.*

Ans. $x=46.34$ Kal. at constant and 8°.

156. Find the heat, x, evolved by the reaction

$$HCl+\tfrac{1}{2}O=\tfrac{1}{2}H_2O+Cl+x \text{ cals.}$$

We know that

$$2H_2+O_2=2H_2O+115{,}600 \text{ cals.},$$

and

$$H_2+Cl_2=2HCl+44{,}000 \text{ cals.}$$

Ans. $x=6900$ cals.

157. What is the heat of formation of a very dilute solution of magnesium chloride. (See text for data.)

Ans. 1875 Kal.

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158. At 279° and 737.2 mm., α for the reaction,

$$2NO_2 \rightleftarrows 2NO + O_2,$$

is 0.13. Find K_p and K_c both for the reaction as written, and also for the form $NO_2 \rightleftarrows NO + O$.

Ans. $K_p = 0.001323$ for $2NO_2$; 0.03639 for NO_2 (p in atmos.)
$K_c = 0.0000292$ for $2NO_2$; 0.0054 for NO_2.

159. At 440° ($K = 0.02$), 5.3 cc. of hydrogen are mixed with 7.94 cc. of iodine vapor. How much hydriodic acid, according to the reaction, $H_2 + I_2 \rightleftarrows 2HI$, is formed?

Ans. 9.475 cc.; obs. 9.52 cc.

160. For the gaseous dissociation $AB \rightleftarrows A + B$, at 100°, α is 0.17, under atmospheric (constant) pressure.

(*a*) Find the extent of the dissociation, when we start with 1 mole of AB at 100°, under the constant pressure of 650 mm.

(*b*) Find α at 100° under the constant pressure of 800 mm., when we start with 1 mole of AB.

Ans. (*a*), $\alpha = 0.1833$;
(*b*), $\alpha = 0.1658$.

161. In (160) assume we start with 0.3 mole of AB, 0.6 of A, and 0.2 of B. Find the direction and extent of the reaction leading to the equilibrium state.

(*a*) When the volume is held constant at that occupied by the original 1.1 moles at 100° and 1 atmospheric pressure.

(*b*) When the pressure is held constant throughout at 1 atmosphere.

Ans. (*a*) 0.165 mole of AB formed.
(*b*) 0.1697 mole of AB formed.

162. In (160) find

(*a*) The value of α when 0.1 mole of A is added to the original 1 mole of AB, before this is allowed to dissociate, and the volume is held constant at what it would be for the 1.1 moles, without reaction, at 100° and atmospheric pressure.

(*b*) Find α, as in (*a*), except that the pressure is assumed to remain constant at 1 atmosphere throughout.

Ans. (*a*) $\alpha=0.1264$;
(*b*) $\alpha=0.1352$.

Compare these results with those in (160), where no addition of A from the exterior was made.

163. In (160) find α, when we start with 1 mole of AB, holding the volume constant at which it would be for the 1 mole without reaction at 100° and atmospheric pressure.

Ans. $\alpha=0.1583$.

Compare this result with those of (160) and (162), under other conditions.

164. For the reaction, $AB \rightleftarrows A+B-100$ Kal., (the value 100 holding at constant volume and between 0° and 150°), α at 100° for constant (atmospheric) pressure conditions is 0.17. Find α at (*a*) 75°; and (*b*) at 125°, both also under constant, atmospheric, pressure.

Ans. (*a*) $\alpha=0.1025$.
(*b*) $\alpha=0.2615$.

Compare these values with the qualitative information given by the application of the theorem of Le Chatelier to this reaction.

165. In (160) assume that we start with a mixture of AB, A and B at 100°, in which the partial pressures before reaction are $p_{AB}=0.3$; $p_A=0.5$; $p_B=0.2$ atmosphere. Find the direction and extent of the reaction carrying the system to the equilibrium state, on the assumption that the volume remains unchanged from what it would be without reaction.

Ans. 0.1597 atmos. of AB formed.

166. At 440° in 50 liters we have a mixture of 2.74 moles of HI, 0.5 mole of H and 0.3011 mole of I. K_c, for the reaction $2HI \rightleftarrows H_2+I_2$, is 0.02 at 440°. In which direction will the reaction go?

167. For the reaction of the Deacon process for chlorine, $HCl+\frac{1}{4}O_2 \rightleftarrows \frac{1}{2}H_2O+\frac{1}{2}Cl_2$, we find K_p at 386° C., is 3.02, and at 419° C., is 2.35. Calculate the heat evolved by the reaction taking place under constant pressure, at a temperature equal to the mean of the two given ones. Ans. 6969 cals.

Compare this result with that of (156).

168. For the reaction $N_2+2H_2O \rightleftarrows 2NO+2H_2$, we find at 2000° C. $K_p=2.5\times10^{-9}$, the partial pressures being expressed in atmospheres. Starting with 0.75 mole of N_2 and 0.25 mole of H_2, find the amount of NO formed by the reaction in going into the equilibrium state, under constant, atmospheric, pressure. (The change here is so small, compared with numbers such as the above, that in the *final* statement of the criterion of equilibrium, the term expressing it may be disregarded as negligible, when added or subtracted.)

Ans. 0.0033 mole of NO formed.

169. For the reaction, $2HCl \rightleftarrows H_2+Cl_2$, we find

$$\log K_p=\frac{-9550}{T}+0.553\log T-2.42.$$

What is the degree of dissociation of hydrochloric acid gas at 1727° C., and atmospheric pressure? Ans. $\alpha=0.00413$.

170. α, for the reaction, $A_3B_2 \rightleftarrows 3A+2B$, at 125° and constant, atmospheric, pressure, is 0.5. Find the direction and extent of the reaction necessary to produce the equilibrium state, when we start with 0.1 atmosphere of A_3B_2, 0.3 of A, and 0.6 of B, and retain the volume constant at that which they would occupy originally (without reaction) at 125° and 1 atmosphere pressure.

Ans. x atmospheres of A_3B_2 are formed, the value of x and its sign being given by the expression $0.44x-4.97x^2+32.4x^3-97.2x^4+105x^5=0.0014$.

(*Note.* If the condition here was to be *constant pressure*, it would be necessary first to transform the original partial pressures into moles per liter by $c=\frac{p}{RT}$, and then to assume 1 liter, and treat the original moles so obtained exactly as we did for the simpler reaction in (160), except for the difference in exponents and coefficients.)

171. The vapor-pressure of water is 4.54 mm. at 0°, and 10.02 at 11.54. Find the heat of evaporation of 1 mole of water at constant pressure.

Ans. $Q_p = -10{,}780$ cals.; obs. $= -10{,}854$ cals.

172. The salt $Na_2HPO_4 \cdot 12H_2O$ has a vapor-pressure (of water vapor), at 15°, equal to 8.84 mm., and at 17°.3, to 10.53 mm. Find the heat evolved by the loss of the water of crystallization of the salt, at constant pressure.

Ans. $Q_p = -12{,}710$ cals.

173. The solid A_2B_3 ($A_2B_3 \rightleftarrows 2A + 3B$) has a dissociation pressure of 2 atmospheres at 100°, the substance A_2B_3 existing practically only as a solid. (*a*) Find the "constant$_p$" which can be treated just as the criterion of equilibrium can be.

Ans. "constant$_p$" $= 1.106$ (p in atmospheres).

(*b*) Assume the A_2B_3 to dissociate at 100° into a space already containing a pressure of the gas A equal to 0.5 atmosphere. How much B will be found?

Ans. $3x$ atmospheres, the value of x being fixed by the equation $108x^5 + 54x^4 + 6.75x^3 = 1.106$.

174. For the reaction $NH_4HS \rightleftarrows H_2S + NH_3$ at 25°.1, constant$_p$" $= 62{,}400$ (for pressures in mm.); the NH_4HS practically existing only as a solid. If in an evacuated space at 25°.1, we introduce NH_3 and H_2S, until we have the partial pressures (without reaction) of 300 and 594 mm., respectively, and allow them to react, how much will each gas lose in pressure?

Ans. 157.2 mm.

175. For the reaction in (174) we find the dissociation pressure to be 175 mm. at 9°.5, and 501 mm. at 25°.1. Find the

heat of dissociation of solid ammonium sulphydrate at constant pressure, and $\left(\frac{25.1+9.5}{2}\right)^\circ$.

Ans. $Q_p = -22{,}780$ cals. per mole; obs. $= 22{,}800$.

176. In the equilibrium state of the reaction,

$$2\ Fe(solid)+4H_2O \rightleftarrows Fe_3O_4(solid)+4H_2,$$

at 200° C., $p_{H_2O}=4.6$ mm. and $p_H=95.9$. Find the equilibrium pressure of hydrogen when that of water vapor is 9.7 mm.

Ans. $p_H=202.2$ mm.

177. For the equilibrium $NH_4CN \rightleftarrows HCN+NH_3$ (where the ammonium cyanide is a solid, not existing as a gas) at 11° the dissociation pressures is 22.7 cm. Find (*a*) the partial pressure of HCN if the solid is allowed to dissociate at 11° in a closed vessel already containing ammonia gas to a pressure of 32.28 cms.; (*b*) what will be the total pressure of the system.

Ans. (*a*) $p_{HCN}=3.59$ cm.; (*b*) $p_{total}=39.46$ cm.

178. Metallic iron (see (176)) is heated with steam at 200° until equilibrium is established at a pressure of 1 atmosphere. Find the final partial pressures of water vapor and of hydrogen.

Ans. $p_{H_2O}=0.0456$ atmos., $p_{H^2}=0.9454$ atmos.

179. In (178) how much NH_4CN will sublime in 1 liter at 11°.2?

Ans. 0.00203 mole.

180. The constant of equilibrium for the reaction of amylene and acetic acid (page 289) is 830.1. At the temperature at which this is true, 2 moles of amylene are mixed with *a* moles of acid in 2 liters, and 0.5 mole of ester is formed. Find *a*, the original number of moles of acid.

Ans. 0.5008.

181. A mixture of 6.63 moles of amylene (page 289) with 1 mole of acid produces 0.838 mole of ester in the total volume of 894 liters. How much ester will be formed if we start with 4.48 moles of amylene and 1 of acid in the volume of 683 liters? The temperature, and hence the value of K, here is different from that in (180).

Ans. 0.8111 mole.

182. Acetic acid distributes between water and benzene so that, in a definite volume of water, we find, in two cases, 0.245 and 0.314 gram, when in an equal volume of benzene we find 0.043 and 0.071 gram respectively. What is the molecular weight of acetic acid in benzene? In water $M_{CH_3COOH} = 60$.

Ans. 2.02×60.

183. After shaking 1000 cc. of a water solution of aniline with 59 cc. of benzene we find that 0.03285 gram of aniline in 50 cc. of the benzene layer, and 0.0647 gram in 1000 cc. of the water layer. Find the coefficient of distribution of aniline between water and benzene. Ans. $\frac{w_{\text{water}}}{w_{\text{benzene}}} = 0.0985$.

184. After distributing succinic acid between water and *ether*, we find in equal volumes (10 cc.) of the two solvents, the following weights (grams) of acid:

In H_2O	In Ether
0.121	0.022
0.070	0.013
0.024	0.0046

After distributing succinic acid between water and *benzene*, we find the following amounts of acid per unit of volume of layer:

In H_2O	In Benzene
0.0150	0.242
0.0195	0.412
0.0289	0.970

Knowing the molecular weight of the acid to be 118 in water solution, find what it is in ether and in benzene solutions.

Ans. *M* in ether = 118.
M in benzene = 236.

185. Starting (*a*) with 1 gram of a substance per liter in solvent (1), and shaking with 50 cc. of solvent (2), find the amount of substance left in the liter of (1) after the extraction (*M* is identical in the two solvents). (*b*) Find the amount of

substance left in the liter of (1), after five successive extractions with 10 cc. each of solvent (2). Previous experiment shows that at equilibrium $\frac{w_1}{w_2}=0.0017$.

Ans. (*a*) 0.0329 gram per liter.
(*b*) 0.00000647 gram per liter.

186. A mixture of alcohol and hydrochloric acid when in equilibrium at 77° gives $K_c=0.307$, while at 99° it gives $K_c=0.177$. Find the heat generated by the reaction.

Ans. $Q_v=+6519$ cals.

187. The speed constant of formation of hydriodic acid, $H_2+I_2 \rightleftarrows 2HI$ is 0.00023 at 374°, while $K_c=0.0157$. What is the speed constant of decomposition of hydriodic acid?

Ans. 0.0147; obs. 0.0140.

188. To 1 liter of a 0.762 molar solution of a monobasic organic acid ($K_c=0.000018$) a salt with an ion in common is added. How much of the negative ion must be in the salt added (when dissolved) to decrease the concentration of H^+ ion to 1/10 of its previous value in pure water, where it is equal to that of the negative ion? Ans. 0.03703 mole per liter.

189. To 1 liter of a solution which contains $\frac{1}{8}$ mole each of two bases ($K_{NH_4OH}=2.3\times10^{-5}$; $K_{NH_2(CN_3)OH}=51.98\times10^{-5}$), we add $\frac{1}{8}$ mole of hydrochloric acid. Find the amount of acid neutralized by each base.

Ans. 0.1033 mole per liter by methylamine.
0.0217 mole per liter by ammonium hydroxide.

190. A small amount of base is mixed with a large amount of a solution containing equi-molecular amounts of acetic and lactic acids. In what proportion will they neutralize the base? (For data, see table on page 323.)

Ans. Acetic : lactic :: 0.00424 : 0.0114.

191. What solution of glycollic acid ($K=15.2\times10^{-5}$) is isohydric with a 0.1 molar solution of acetic acid ($K=1.8\times10^{-5}$)?

Ans. $v_m=84.4$ liters; $c=0.01184$ molar.

192. The constant for the first hydrogen ion of malonic acid ($K = k_1$) is 158×10^{-5}, that for the second (k_2) is 1×10^{-6}. What is the total concentration of H^+ ion, from both stages, in a solution of malonic acid which contains 1 mole in 2000 liters? Ans. c_{H^+}(total) $= 0.00042$ mole per liter.

193. The degree of ionization, α, for KCl in solution is 0.7167 for $v_m = 1$; 0.9052 for $v_m = 32$; and 0.9134 for $v_m = 64$. Calculate the values of the constant by the dilution laws of Ostwald, Rudolphi and van't Hoff, and show that the former fails utterly to hold.

194. The value of K, as found from a 0.05 molar solution of acetic acid is 0.0000175 at 18°, and 0.00001624 at 52°. What is the heat of ionization of acetic acid? At what temperature would this be true? Ans. $+415.2$ cals. at 35°.

195. Find the heat of neutralization of 1 mole of acetic acid (in 200 moles of H_2O) with 1 mole of sodium hydroxide (in 200 moles of H_2O) at 35°; α for acetic acid is 0.009 at this concentration, the heat of ionization is 386 cals.; α for NaOH is 0.861, its heat of ionization is 1292 cals.; and α for the sodium acetate formed is 0.742, its heat of ionization being 391 cals., while the heat of formation of water from H^+ and OH^- is 12,632 cals. Ans. 13,093 cals.

196. The solubility of succinic acid in water at 0° is 2.88, while at 8°.5 it is 4.22, both in the same definite molar units, per liter. Ignoring the slight ionization of succinic acid at this concentration of solution, find the heat of solution, per mole, of succinic acid. Ans. $Q_v = -6911$ cals.; obs. $= -6700$ cals.

197. The solubility of AgCl ($\alpha = 1$, into $Ag^+ + Cl^-$) is 1.1×10^{-5} at 20°, and $1.73 + 10^{-5}$ at 30°. Find the heat of solution of 1 mole of AgCl, forming 1 mole each of Ag^+ and Cl^- ion. Ans. $= -16{,}080$ cals.

The heat of precipition of AgCl from $Ag^+ + Cl^-$ was found on page 244, it will be remembered, to be 15,800 cals. by an entirely different method.

198. The solubility of $BaSO_4$ at 37°.7 is 1 mole in 31,283 liters. What is its solubility product at this temperature, on the assumption that it is completely ionized? Ans. 1.02×10^{-9}.

199. At 18°.4 1 mole of $BaSO_4$ dissolves in 50,055 liters, while at 37°.7 it dissolves in 31,283 liters. On the justified assumption that it is completely ionized in these dilutions, find the heat of ionization, i.e., the heat produced when 1 mole of $BaSO_4$ dissolves and produces 1 mole each of Ba^{++} and $SO_4^{=}$ ion.

Ans. $Q_v = -8822$ cals.

200. PbI_2 is soluble to 0.00158 mole per liter at 25°.2, and is completely ionized into $Pb^{++} + 2I^-$. What is the solubility of lead iodide in a solution which already contains 0.1 mole per liter of I^- ion from another source?

Ans. 1.58×10^{-6} mole per liter.

201. Water under atmospheric pressure at 16° absorbs 0.0753 liter of CO_2 per liter, i.e., 0.04354 mole per liter. Of this 0.000115 mole (0.264%) is ionized into H^+ and HCO_3^- ions. What is the solubility product, considering that the ionization takes place in this way? Ans. 1.32×10^{-8}.

202. $s_{AB} = 5.5 \times 10^{-10}$. Find c_A and c_B in a saturated solution of AB which is completely ionized.

Ans. $c_A = c_B = 2.35 \times 10^{-5}$.

203. The solubility product of the substance AC_2 $(= A^{++} + 2C^-)$ is 6.21×10^{-6}. Find the concentrations of A^{++} and C^- ions in a saturated solution, assuming the ionization to be complete.

Ans. $c_{A^{++}} = 0.01158$; $c_{C^-} = 0.02316$ mole per liter.

204. AgCNO $(= Ag^+ + CNO^-)$ is soluble at 100° to 0.008 mole per liter. How much will dissolve in a solution already containing 0.1 mole per liter of Ag^+ ion from another source?

Ans. 6.4×10^{-4} mole per liter.

205. The solubility of $Mg(OH)_2$ $(= Mg^{++} + 2OH^-, \alpha = 1)$ is 0.00002 mole per liter, There are 1.5 moles of NH_4^+ ion from NH_4Cl, and 0.0001 mole per liter of Mg^{++} (from the chloride)

present in a molar solution of NH_4OH ($K = 0.000023$); find the concentration of OH^- ion that must be added to the solution to just cause the solubility product of $Mg(OH)_2$ to be attained.

Ans. 0.26×10^{-5}.

206. At 25°, the solubility of AgBr ($\alpha = 1$, $Ag^+ + Br^-$) is 86×10^{-8}, and of AgI ($\alpha = 1$, $Ag^+ + I^-$) is 0.97×10^{-8}. How much Br^+ ion must be added, before precipitation of AgBr, from a saturated solution of AgI, is started? Ans. 7.63×10^{-5}.

207. A mixture of silver chloride, bromide and iodide in the dry state is dissolved in water. How much of each will dissolve, in moles per liter, knowing that in all cases $\alpha = 1$? The solubility of AgCl is 1.25×10^{-5}, while those of the others are given in (206).

Ans. $c_{AgCl} = 1.248 \times 10^{-5}$; $c_{AgBr} = 5.9 \times 10^{-8}$;
$c_{AgI} = 0.00075 \times 10^{-8}$.

208. Brom-iso-cinnamic acid at 25° is soluble to 0.0176 mole per liter, and is ionized in the saturated solution to the extent of 1.76% into H^+ and a negatively charged ion. What is its solubility product? Ans. 9.6×10^{-8}.

209. How much of the acid (208) must always remain in solution, even in the presence of an infinite amount of H^+ from another acid? Ans. 0.0173 mole per liter.

210. What is the *total* solubility of brom-iso-cynnamic acid (208) and (209) in the presence of 0.001 mole per liter of H^+ ion from another acid?

Ans. Total solubility $= 0.0173 + 0.0000883$ mole per liter.

211. Aniline distributes between water and ether so that there is always 10.1 times as much in a definite volume of the ether layer as in an equal volume of the water layer. Starting with 0.03138 mole per liter of aniline hydrochloride, and shaking this liter of water solution with 59 cc. of ether, we find 0.02916 gram of aniline in 50 cc. of the ether layer. Find the hydrolytic dissociation of aniline hydrochloride in the water solution.

Ans. 2.6%.

212. The constant of hydrolytic dissociation at 100° for NH_4Cl is 337×10^{-10} $\left(\text{i.e., constant} = \frac{\alpha^2}{(1-\alpha)v_m} \cdot \frac{d_A}{d_s}\right)$. What is the ionization constant of NH_4OH? $s_{H_2O} = (8.5 \times 10^{-7})^2$? $(d_A = d_S = 1)$. Ans. 214×10^{-7}.

213. At 25° aniline acetate, $v_m = 195.9$, is 52.3% hydrolyzed into aniline hydrate and acetic acid, both very slightly ionized. The unhydrolyzed salt (v_m about 400) is 95.3% ionized; $s_{H_2O} = (1.09 \times 10^{-7})^2$; $K_{HA} = 0.000018$. Find ionization constant $\left(\frac{c_M c_{OH}}{c_{MOH}}\right)$ of aniline hydrate. Ans. 4.99×10^{-10}.

214. The concentration of the salt MA_4 $(= M^{++++} + 4A^-$, $\alpha = 0.6)$ is 0.0001 mole per liter. The base $M(OH)_4$ $(= M^{++++} + 4OH^-)$ is soluble only to 0.00001 mole per liter, but is then completely ionized. Will the salt in this concentration dissociate hydrolytically in water at 25°, for which $s_{H_2O} = (0.91 \times 10^{-7})^2$? Ans. No.

215. At a dilution of 32 liters the binary salt is 0.9% hydrolyzed. What is its percentage of hydrolysis at 100 liters, assuming complete ionozation of the salt left and of the acid formed? Ans. 1.584%.

216. K for cinnamic acid (acting as a monobasic acid) at 25° is 0.0000345, and its solubility in water is 0.00331 mole per liter, the ionization in this saturated solution being 9.84%. In a 0.01 molar solution of aniline in water (forming by the reaction a base) the solubility is increased to 0.00804 mole per liter. The salt formed here is 93% ionized and $s_{H_2O} = (1.09 \times 10^{-7})^2$. Find the ionization constant

$$\left(K = \frac{c_M c_{OH}}{c_{MOH}}\right) \text{ for aniline.}$$

Ans. $c_{MA} = 0.000331$. $c_{M^+} = 0.0047$.
$c_{OH^-} = 5.5 \times 10^{-10}$. $c_{MOH} = 0.00496$.
$c_{HA} = 0.00298$. $K = 5.2 \times 10^{-10}$.
$c_{H^+} = 0.0000217$.

Compare this value of K with that from (213) by the reverse reaction of hydrolytic dissociation.

ELECTROCHEMISTRY

217. An aqueous solution of copper sulphate is electrolyzed until 0.2955 gram of metallic copper is deposited, using inert electrodes. The volume of liquid at the cathode before the passage of current contained 2.2762 grams of copper, and after the passage, 2.065 grams. Find the transport numbers of Cu^{++} and $SO_4^{=}$ ions. Ans. $n_{Cu^{++}} = 0.285$; $n_{SO_4^{=}} = 0.715$.

218. An aqueous solution of copper sulphate is electrolyzed with copper electrodes until 0.2294 gram of copper is deposited. Before electrolysis the volume of solution around the anode contained 1.195 grams of copper, after electrolysis 1.360 grams. Find the transport numbers of Cu^{++} and $SO_4^{=}$ as ion.

Ans. $n_{Cu^{++}} = 0.281$; $n_{SO_4^{=}} = 0.719$.

219. A 0.02 normal solution of potassium chloride ($\kappa_{18^\circ} = 0.002397$) gives in a certain electrolytic cell a resistance of 150 ohms. Find the factor which will transform the results for conductivity in this cell directly into *specific* conductivity.

Ans. 0.359.

220. Find the ionization constant, according to the law of mass action, of ammonium hydroxide. The equivalent conductivity observed, for various dilutions, at a certain temperature are: $\Lambda_8 = 3.4$; $\Lambda_{16} = 4.8$; $\Lambda_{32} = 6.7$; $\Lambda_{64} = 9.5$; $\Lambda_{128} = 13.5$; $\Lambda_{256} = 18.2$. Further, the following values of the equivalent conductivity at infinite dilution are found: Λ_∞ for $NH_4Cl = 130.1$; Λ_∞ for $KOH = 239.3$; and Λ_∞ for $KCl = 131.2$.

Ans. $K = \dfrac{c_{NH_4}c_{OH}}{c_{NH_4OH}} = 0.0000257$ in average.

221. At 18°, lactic acid gives the following values: $\Lambda_{32} = 23.11$; $\Lambda_{64} = 32.21$; $\Lambda_{128} = 44.47$; $\Lambda_{256} = 60.23$; $\Lambda_{512} = 82.2$; and $\Lambda_{1024} = 116.9$. What is the ionization constant of lactic acid (considered as monobasic) according to the law of mass

action? Λ_∞ for HCl = 383.9; Λ_∞ for NaCl = 110.3; and Λ_∞ for the mono sodium salt of lactic acid = 85.1.

Ans. Average $K = \frac{c_H c_A}{c_{HA}} = 0.000136$.

222. The velocity of migration of Ag^+ ion is 0.00057 cm. per second, as is also that for ClO_3^-. What is the equivalent conductivity of a solution of $AgClO_3$ which is infinitely dilute?

Ans. 110.

223. The equivalent conductivity of the sodium salt of an acid is $\Lambda_{32} = 89.9$; $\Lambda_{64} = 97.1$; $\Lambda_{128} = 104.5$; $\Lambda_{256} = 111.1$; $\Lambda_{512} = 117.2$; and $\Lambda_{1024} = 122.7$. What is the basicity of the acid.

Ans. Tri-basic.

224. The equivalent conductivity of a solution of 1 equivalent of $Na_2SO_4(2\ Na^{++} + SO_4^{=})$ in 100 liters of water at 25° is 134.9. What is the equivalent conductivity at infinite dilution? (See data in text.)

Ans. $\Lambda_\infty = 153.9$.

225. At 25° the specific conductivity of ethylamine at a dilution of 1 equivalent in 16 liters is 1.312×10^{-3} reciprocal ohms. The equivalent conductivity at infinite dilution is 232.6. Find the ionization constant of the law of mass action, considering this base as a binary electrolyte, for it behaves as ammonia does when dissolved in water.

Ans. 5.6×10^{-4}.

226. The specific conductivity of a water solution of silver chloride, saturated at 18°, is 2.4×10^{-6} reciprocal ohms; while that of the water itself, used in making the solution, is 1.16×10^{-6}. Calculate the solubility of silver chloride. $\Lambda_{\infty KCl} = 131.2$; $\Lambda_{\infty AgNO_3} = 116.5$; and $\Lambda_{\infty KNO_3} = 126.1$.

Ans. 1.02×10^{-5} mole per liter.

227. At 25°, $v_m = 99.2$, Λ for aniline hydrochloride is 118.6; while Λ for aniline hydrochloride, plus an excess of aniline, is 103.6. Λ_{HCl} ($v_m = 99.2$) is 411. Here the conductivity of aniline itself is negligibly small. Find the degree of hydrolytic dissociation, and the constant for hydrolytic dissociation.

Ans. $\alpha = 0.0488$; $K_{hyd.} = 2.52 \times 10^{-5}$.

228. Find the heat of amalgamation of cadmium at 12°.23. E, for a cell made up of an electrode of a 1% cadmium amalgam on the one side, and mercury on the other, in a solution of cadmium sulphate, is 0.06836 volt at 0°, and 0.0735 volt at 24°.45.

Ans. $Q = 506.6$ cals. per mole of Cd.

229. Zinc in a molar zinc sulphate solution gives a difference of potential of 0.51 volt, and a value of $\frac{\Delta E}{\Delta T} = -0.00076$ volt. What is the heat of ionization of zinc at 17°?

Ans. 336.9 Kal.

230. $Zn + 2H^+ + Cl^- + Aq = Zn^{++} + 2Cl^= + Aq + H_2 + 342$ Kal. and from (229) $Zn = Zn^{++} + 337.4$ Kal. What is the heat of ionization of gaseous hydrogen? Ans. $H_2 = 2H^+ - 5.1$ Kal.

231. A potassium cyanide solution is added to the copper side of a Daniell cell, and as a result the electromotive force of the cell becomes zero. What conclusion is to be drawn?

232. A single electrode, in connection with the normal electrode ($E = -0.56$) gives an electromotive force of 1.02 volts, the normal electrode being positive. What is the difference of potential between the single electrode and its solution?

Ans. $\epsilon = 0.46$, i.e., the metal is negative against the solution.

233. A cell with electrodes of the same univalent metal gives an electromotive force at 17° of 0.35 volt. The concentration of metal ion at the positive electrode is 0.02 mole per liter. What is the ionic concentration on the other side?

Ans. 1.84×10^{-8} mole per liter.

234. Find the electromotive force, at 25°, of the cell: H gas – KOH N/10 ($\alpha = 0.85$) – N/10 HCl($\alpha = 0.7$) H gas, $s_{H_2O} = (1.09 \times 10^{-7})^2$. Ans. 0.757 volt.

235. Find the concentration of OH^- ion. The cell

H gas – base———N/10 HCl($\alpha = 0.7$)H gas,

gives an electromotive force of 0.8 volt at 25°. $s_{H_2O} = (1.09 \times 10^{-7})^2$. Ans. $c_{H^+} = 2.6 \times 10^{-14}$.

$c_{OH^-} = 0.457$.

236. A cell with electrodes of a divalent metal, with the ionic concentrations on the two sides equal to 0.02 and 1.84×10^{-8} mole per liter. What is the electromotive force of the cell at 17°? Ans. 0.175 volt.

237. In a gas cell with hydrogen electrodes there is acetic acid on one side, and propionic acid on the other, both of the same concentration. What is the electromotive force of the cell at 25°? Which pole is positive? (For data, see table, page 323.) Ans. $E = 0.00382$ volt, acetic acid side positive.

238. In the above cell (237), the pressure of hydrogen gas is increased to ten times its value on both electrodes. How does the electromotive force change?

No.	0	1	2	3	4	5	6	7	8	9	1	2	3	4	5	6	7	8	9
10	0000	0043	0086	0128	0170	0212	0253	0294	0334	0374	4	8	12	17	21	25	29	33	37
11	0414	0453	0492	0531	0569	0607	0645	0682	0719	0755	4	8	11	15	19	23	26	30	34
12	0792	0828	0864	0899	0934	0969	1004	1038	1072	1106	3	7	10	14	17	21	24	28	31
13	1139	1173	1206	1239	1271	1303	1335	1367	1399	1430	3	6	10	13	16	19	23	26	29
14	1461	1492	1523	1553	1584	1614	1644	1673	1703	1732	3	6	9	12	15	18	21	24	27
15	1761	1790	1818	1847	1875	1903	1931	1959	1987	2014	3	6	8	11	14	17	20	22	25
16	2041	2068	2095	2122	2148	2175	2201	2227	2253	2279	3	5	8	11	13	16	18	21	24
17	2304	2330	2355	2380	2405	2430	2455	2480	2504	2529	2	5	7	10	12	15	17	20	22
18	2553	2577	2601	2625	2648	2672	2695	2718	2742	2765	2	5	7	9	12	14	16	19	21
19	2788	2810	2833	2856	2878	2900	2923	2945	2967	2989	2	4	7	9	11	13	16	18	20
20	3010	3032	3054	3075	3096	3118	3139	3160	3181	3201	2	4	6	8	11	13	15	17	19
21	3222	3243	3263	3384	3304	3324	3345	3365	3385	3404	2	4	6	8	10	12	14	16	18
22	3424	3444	3464	3483	3502	3522	3541	3560	3579	3598	2	4	6	8	10	12	14	15	17
23	3617	3636	3655	3674	3692	3711	3729	3747	3766	3784	2	4	6	7	9	11	13	15	17
24	3802	3820	3838	3856	3874	3892	3909	3927	3945	3962	2	4	5	7	9	11	12	14	16
25	3979	3997	4014	4031	4048	4065	4082	4099	4116	4133	2	3	5	7	9	10	12	14	15
26	4150	4166	4183	4200	4216	4232	4249	4265	4281	4298	2	3	5	7	8	10	11	13	15
27	4314	4330	4346	4362	4378	4393	4409	4425	4440	4456	2	3	5	6	8	9	11	13	14
28	4472	4487	4502	4518	4533	4548	4564	4579	4594	4609	2	3	5	6	8	9	11	12	14
29	4624	4639	4654	4669	4683	4698	4713	4728	4742	4757	1	3	4	6	7	9	10	12	13
30	4771	4786	4800	4814	4829	4843	4857	4871	4886	4900	1	3	4	6	7	9	10	11	13
31	4914	4928	4942	4955	4969	4983	4997	5011	5024	5038	1	3	4	6	7	8	10	11	12
32	5051	5065	5079	5092	5105	5119	5132	5145	5159	5172	1	3	4	5	7	8	9	11	12
33	5185	5198	5211	5224	5237	5250	5263	5276	5289	5302	1	3	4	5	6	8	9	10	12
34	5315	5328	5340	5353	5366	5378	5391	5403	5416	5428	1	3	4	5	6	8	9	10	11
35	5441	5453	5465	5478	5490	5502	5514	5527	5539	5551	1	2	4	5	6	7	9	10	11
36	5563	5575	5587	5599	5611	5623	5635	5647	5658	5670	1	2	4	5	6	7	8	10	11
37	5682	5694	5705	5717	5729	5740	5752	5763	5775	5786	1	2	3	5	6	7	8	9	10
38	5798	5809	5821	5832	5843	5855	5866	5877	5888	5899	1	2	3	5	6	7	8	9	10
39	5911	5922	5933	5944	5955	5966	5977	5988	5999	6010	1	2	3	4	5	7	8	9	10
40	6021	6031	6042	6053	6064	6075	6085	6096	6107	6117	1	2	3	4	5	6	8	9	10
41	6128	6138	6149	6160	6170	6180	6191	6201	6212	6222	1	2	3	4	5	6	7	8	9
42	6232	6243	6253	6263	6274	6284	6294	6304	6314	6325	1	2	3	4	5	6	7	8	9
43	6335	6345	6355	6365	6375	6386	6395	6405	6415	6425	1	2	3	4	5	6	7	8	9
44	6435	6444	6454	6464	6474	6484	6493	6503	6513	6522	1	2	3	4	5	6	7	8	9
45	6532	6542	6551	6561	6571	6580	6590	6599	6609	6618	1	2	3	4	5	6	7	8	9
46	6628	6637	6646	6656	6665	6675	6684	6693	6702	6712	1	2	3	4	5	6	7	7	8
47	6721	6730	6739	6749	6758	6767	6776	6785	6794	6803	1	2	3	4	5	5	6	7	8
48	6812	6821	6830	6839	6848	6857	6866	6875	6884	6893	1	2	3	4	4	5	6	7	8
49	6902	6911	6920	6928	6937	6946	6955	6964	6972	6981	1	2	3	4	4	5	6	7	8
50	6990	6998	7007	7016	7024	7033	7042	7050	7059	7067	1	2	3	3	4	5	6	7	8
51	7076	7084	7093	7101	7110	7118	7126	7135	7143	7152	1	2	3	3	4	5	6	7	8
52	7160	7168	7177	7185	7193	7202	7210	7218	7226	7235	1	2	2	3	4	5	6	7	7
53	7243	7251	7259	7267	7275	7284	7292	7300	7308	7316	1	2	2	3	4	5	6	6	7
54	7324	7332	7340	7348	7356	7364	7372	7380	7388	7396	1	2	2	3	4	5	6	6	7
	0	1	2	3	4	5	6	7	8	9	1	2	3	4	5	6	7	8	9

No.	0	1	2	3	4	5	6	7	8	9	1	2	3	4	5	6	7	8	9
55	7404	7412	7419	7427	7435	7443	7451	7459	7466	7474	1	2	2	3	4	5	5	6	7
56	7482	7490	7497	7505	7513	7520	7528	7536	7543	7551	1	2	2	3	4	5	5	6	7
57	7559	7566	7574	7582	7589	7597	7604	7612	7619	7627	1	2	2	3	4	5	5	6	7
58	7634	7642	7649	7657	7664	7672	7679	7686	7694	7701	1	1	2	3	4	4	5	6	7
59	7709	7716	7723	7731	7738	7745	7752	7760	7767	7774	1	1	2	3	4	4	5	6	7
60	7782	7789	7796	7803	7810	7818	7825	7832	7839	7846	1	1	2	3	4	4	5	6	6
61	7853	7860	7868	7875	7882	7889	7896	7903	7910	7917	1	1	2	3	4	4	5	6	6
62	7924	7931	7938	7945	7952	7959	7966	7973	7980	7987	1	1	2	3	3	4	5	6	6
63	7993	8000	8007	8014	8021	8028	8035	8041	8048	8055	1	1	2	3	3	4	5	5	6
64	8062	8069	8075	8082	8089	8096	8102	8109	8116	8122	1	1	2	3	3	4	5	5	6
65	8129	8136	8142	8149	8156	8162	8169	8176	8182	8189	1	1	2	3	3	4	5	5	6
66	8195	8202	8209	8215	8222	8228	8235	8241	8248	8254	1	1	2	3	3	4	5	5	6
67	8261	8267	8274	8280	8287	8293	8299	8306	8312	8319	1	1	2	3	3	4	5	5	6
68	8325	8331	8338	8344	8351	8357	8363	8370	8376	8382	1	1	2	3	3	4	4	5	6
69	8388	8395	8401	8407	8414	8420	8426	8432	8439	8445	1	1	2	2	3	4	4	5	6
70	8451	8457	8463	8470	8476	8482	8488	8494	8500	8506	1	1	2	2	3	4	4	5	6
71	8513	8519	8525	8531	8537	8543	8549	8555	8561	8567	1	1	2	2	3	4	4	5	5
72	8573	8579	8585	8591	8597	8603	8609	8615	8621	8627	1	1	2	2	3	4	4	5	5
73	8633	8639	8645	8651	8657	8663	8669	8675	8681	8686	1	1	2	2	3	4	4	5	5
74	8692	8698	8704	8710	8716	8722	8727	8733	8739	8745	1	1	2	2	3	4	4	5	5
75	8751	8756	8762	8768	8774	8779	8785	8791	8797	8802	1	1	2	2	3	3	4	5	5
76	8808	8814	8820	8825	8831	8837	8842	8848	8854	8859	1	1	2	2	3	3	4	5	5
77	8865	8871	8876	8882	8887	8893	8899	8904	8910	8915	1	1	2	2	3	3	4	4	5
78	8921	8927	8932	8938	8943	8949	8954	8960	8965	8971	1	1	2	2	3	3	4	4	5
79	8976	8982	8987	8993	8998	9004	9009	9015	9020	9025	1	1	2	2	2	3	4	4	5
80	9031	9036	9042	9047	9053	9058	9063	9069	9074	9079	1	1	2	2	3	3	4	4	5
81	9085	9090	9096	9101	9106	9112	9117	9122	9128	9133	1	1	2	2	3	3	4	4	5
82	9138	9143	9149	9154	9159	9165	9170	9175	9180	9186	1	1	2	2	3	3	4	4	5
83	9191	9196	9201	9206	9212	9217	9222	9227	9232	9238	1	1	2	2	3	3	4	4	5
84	9243	9248	9253	9258	9263	9269	9274	9279	9284	9289	1	1	2	2	3	3	4	4	5
85	9294	9299	9304	9309	9315	9320	9325	9330	9335	9340	1	1	2	2	3	3	4	4	5
86	9345	9350	9355	9360	9365	9370	9375	9380	9385	9390	1	1	2	2	3	3	4	4	5
87	9395	9400	9405	9410	9415	9420	9425	9430	9435	9440	0	1	1	2	2	3	3	4	4
88	9445	9450	9455	9460	9465	9469	9474	9479	9484	9489	0	1	1	2	2	3	3	4	4
89	9494	9499	9504	9509	9513	9518	9523	9528	9533	9538	0	1	1	2	2	3	3	4	4
90	9542	9547	9552	9557	9562	9566	9571	9576	9581	9586	0	1	1	2	2	3	3	4	4
91	9590	9595	9600	9605	9609	9614	9619	9624	9628	9633	0	1	1	2	2	3	3	4	4
92	9638	9643	9647	9652	9657	9661	9666	9671	9675	9680	0	1	1	2	2	3	3	4	4
93	9685	9689	9694	9699	9703	9708	9713	9717	9722	9727	0	1	1	2	2	3	3	4	4
94	9731	9736	9741	9745	9750	9754	9759	9763	9768	9773	0	1	1	2	2	3	3	4	4
95	9777	9782	9786	9791	9795	9800	9805	9809	9814	9818	0	1	1	2	2	3	3	4	4
96	9823	9827	9832	9836	9841	9845	9850	9854	9859	9863	0	1	1	2	2	3	3	4	4
97	9868	9872	9877	9881	9886	9890	9894	9899	9903	9908	0	1	1	2	2	3	3	4	4
98	9912	9917	9921	9926	9930	9934	9939	9943	9948	9952	0	1	1	2	2	3	3	4	4
99	9956	9961	9965	9969	9974	9978	9983	9987	9991	9996	0	1	1	2	2	3	3	3	4
	0	1	2	3	4	5	6	7	8	9	1	2	3	4	5	6	7	8	9

Log.	0	1	2	3	4	5	6	7	8	9	1	2	3	4	5	6	7	8	9
.00	1000	1002	1005	1007	1009	1012	1014	1016	1019	1021	0	0	1	1	1	1	2	2	2
.01	1023	1026	1028	1030	1033	1035	1038	1040	1042	1045	0	0	1	1	1	1	2	2	2
.02	1047	1050	1052	1054	1057	1059	1062	1064	1067	1069	0	0	1	1	1	1	2	2	2
.03	1072	1074	1076	1079	1081	1084	1086	1089	1091	1094	0	0	1	1	1	1	2	2	2
.04	1096	1099	1102	1104	1107	1109	1112	1114	1117	1119	0	1	1	1	1	2	2	2	2
.05	1122	1125	1127	1130	1132	1135	1138	1140	1143	1146	0	1	1	1	1	2	2	2	2
.06	1148	1151	1153	1156	1159	1161	1164	1167	1169	1172	0	1	1	1	1	2	2	2	2
.07	1175	1178	1180	1183	1186	1189	1191	1194	1197	1199	0	1	1	1	1	2	2	2	2
.08	1202	1205	1208	1211	1213	1216	1219	1222	1225	1227	0	1	1	1	1	2	2	2	3
.09	1230	1233	1236	1239	1242	1245	1247	1250	1253	1256	0	1	1	1	1	2	2	2	3
.10	1259	1262	1265	1268	1271	1274	1276	1279	1282	1285	0	1	1	1	1	2	2	2	3
.11	1288	1291	1294	1297	1300	1303	1306	1309	1312	1315	0	1	1	1	2	2	2	2	3
.12	1318	1321	1324	1327	1330	1334	1337	1340	1343	1346	0	1	1	1	2	2	2	2	3
.13	1349	1352	1355	1358	1361	1365	1368	1371	1374	1377	0	1	1	1	2	2	2	3	3
.14	1380	1384	1387	1390	1393	1396	1400	1403	1406	1409	0	1	1	1	2	2	2	3	3
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23	3617	3636	3655	3674	3692	3711	3729	3747	3766	3784	2	4	6	7	9	11	13	15	17
24	3802	3820	3838	3856	3874	3892	3909	3927	3945	3962	2	4	5	7	9	11	12	14	16
25	3979	3997	4014	4031	4048	4065	4082	4099	4116	4133	2	3	5	7	9	10	12	14	15
26	4150	4166	4183	4200	4216	4232	4249	4265	4281	4298	2	3	5	7	8	10	11	13	15
27	4314	4330	4346	4362	4378	4393	4409	4425	4440	4456	2	3	5	6	8	9	11	13	14
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29	4624	4639	4654	4669	4683	4698	4713	4728	4742	4757	1	3	4	6	7	9	10	12	13
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31	4914	4928	4942	4955	4969	4983	4997	5011	5024	5038	1	3	4	6	7	8	10	11	12
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37	5682	5694	5705	5717	5729	5740	5752	5763	5775	5786	1	2	3	5	6	7	8	9	10
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41	6128	6138	6149	6160	6170	6180	6191	6201	6212	6222	1	2	3	4	5	6	7	8	9
42	6232	6243	6253	6263	6274	6284	6294	6304	6314	6325	1	2	3	4	5	6	7	8	9
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47	6721	6730	6739	6749	6758	6767	6776	6785	6794	6803	1	2	3	4	5	5	6	7	8
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74	8692	8698	8704	8710	8716	8722	8727	8733	8739	8745	1	1	2	2	3	4	4	5	5
75	8751	8756	8762	8768	8774	8779	8785	8791	8797	8802	1	1	2	2	3	3	4	5	5
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92	9638	9643	9647	9652	9657	9661	9666	9671	9675	9680	0	1	1	2	2	3	3	4	4
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94	9731	9736	9741	9745	9750	9754	9759	9763	9768	9773	0	1	1	2	2	3	3	4	4
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ANTILOGARITHMS

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.73	5370	5383	5395	5408	5420	5433	5445	5458	5470	5483	1	3	4	5	6	8	9	10	11
.74	5495	5508	5521	5534	5546	5559	5572	5585	5598	5610	1	3	4	5	6	8	9	10	12
.75	5623	5636	5649	5662	5675	5689	5702	5715	5728	5741	1	3	4	5	7	8	9	10	12
.76	5754	5768	5781	5794	5808	5821	5834	5848	5851	5875	1	3	4	5	7	8	9	11	12
.77	5888	5902	5916	5929	5943	5957	5970	5984	5998	6012	1	3	4	5	7	8	10	11	12
.78	6026	6039	6053	6067	6081	6095	6109	6124	6138	6152	1	3	4	6	7	8	10	11	13
.79	6166	6180	6194	6209	6223	6237	6252	6266	6281	6295	1	3	4	6	7	9	10	11	13
.80	6310	6324	6339	6353	6368	6383	6397	6412	6427	6442	1	3	4	6	7	9	10	12	13
.81	6457	6471	6486	6501	6516	6531	6546	6561	6577	6592	2	3	5	6	8	9	11	12	14
.82	6607	6622	6637	6653	6668	6683	6699	6714	6730	6745	2	3	5	6	8	9	11	12	14
.83	6761	6776	6792	6808	6823	6839	6855	6871	6887	6902	2	3	5	6	8	9	11	13	14
.84	6918	6934	6950	6966	6982	6998	7015	7031	7047	7063	2	3	5	6	8	10	11	13	15
.85	7079	7096	7112	7129	7145	7161	7178	7194	7211	7228	2	3	5	7	8	10	12	13	15
.86	7244	7261	7278	7295	7311	7328	7345	7362	7379	7396	2	3	5	7	8	10	12	13	15
.87	7413	7430	7447	7464	7482	7499	7516	7534	7551	7568	2	3	5	7	9	10	12	14	16
.88	7586	7603	7621	7638	7656	7674	7691	7709	7727	7745	2	4	5	7	9	11	12	14	16
.89	7762	7780	7798	7816	7834	7852	7870	7889	7907	7925	2	4	5	7	9	11	13	14	16
.90	7943	7962	7980	7998	8017	8035	8054	8072	8091	8110	2	4	6	7	9	11	13	15	17
.91	8128	8147	8166	8185	8204	8222	8241	8260	8279	8299	2	4	6	8	9	11	13	15	17
.92	8318	8337	8356	8375	8395	8414	8433	8453	8472	8492	2	4	6	8	10	12	14	15	17
.93	8511	8531	8551	8570	8590	8610	8630	8650	8670	8690	2	4	6	8	10	12	14	16	18
.94	8710	8730	8750	8770	8790	8810	8831	8851	8872	8892	2	4	6	8	10	12	14	16	18
.95	8913	8933	8954	8974	8995	9016	9036	9057	9078	9099	2	4	6	8	10	12	15	17	19
.96	9120	9141	9162	9183	9204	9226	9247	9268	9290	9311	2	4	6	8	11	13	15	17	19
.97	9333	9354	9376	9397	9419	9441	9462	9484	9506	9528	2	4	7	9	11	13	15	17	20
.98	9550	9572	9594	9616	9638	9661	9683	9705	9727	9750	2	4	7	9	11	13	16	18	20
.99	9772	9795	9817	9840	9863	9886	9908	9931	9944	9977	2	5	7	9	11	14	16	18	20
	0	1	2	3	4	5	6	7	8	9	1	2	3	4	5	6	7	8	9

ROYAL ARMY MEDICAL